SOLUBILITIES OF BASES AND SALTS IN WATER AT 18°.

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	$0.0_3$13 $0.0_6$9	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	$0.0_4$1 $0.0_6$6	0.042 $0.0_3$15	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	$0.0_6$35 $0.0_7$1	0.006 $0.0_3$17	201.4 3.8	169.2 3.9	200.0 4.8	148.2 4.1	419.0 6.9	0.08 $0.0_2$2
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3.0	0.16 $0.0_2$92	0.012 0.001	0.0016 $0.0_3$2	0.0087 $0.0_2$14	0.005 $0.0_3$5	0.06 0.002
NO_3	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.35	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO_3	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	3.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO_3	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO_3	7.62 0.35	8.33 0.4	80.43 3.84	0.004 $0.0_3$14	0.059 $0.0_2$16	0.05 0.001	0.25 $0.0_2$57	0.25 0.007	6.87 0.26	0.83 0.02	0.002 $0.0_4$3
OH	142.9 18.0	116.4 21.0	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 0.02	0.001 $0.0_3$2	$0.0_3$5 $0.0_4$5	0.01 $0.0_3$4
SO_4	11.11 0.62	16.83 1.15	34.64 2.8	0.55 0.020	4.74 0.09	$0.0_3$23 $0.0_4$10	0.011 $0.0_3$6	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 $0.0_3$13
CrO_4	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 $0.0_3$15	0.006 $0.0_3$1	$0.0_3$35 $0.0_4$14	0.12 0.006	0.4 0.03	73.0 4.3	....	$0.0_4$2 $0.0_6$5
C_2O_4	30.27 1.6	3.34 0.24	7.22 0.69	0.0034 $0.0_3$17	1.48 0.030	0.0085 $0.0_3$38	0.0046 $0.0_3$26	$0.0_3$55 $0.0_4$43	0.03 0.0027	$0.0_3$64 $0.0_4$4	$0.0_3$16 $0.0_6$54
CO_3	108.0 5.9	19.39 1.8	1.3 0.17	0.003 $0.0_3$1	4.95 0.10	0.0023 $0.0_3$11	0.0011 $0.0_4$7	0.0013 $0.0_3$13	0.1 0.01	0.004? $0.0_3$3?	$0.0_3$1 $0.0_4$3

The ***upper number*** in each square gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The ***lower number*** is the molar solubility, *i.e.*, the number of moles contained in one liter of the saturated solution. The numbers for small solubilities have been abbreviated. Thus $0.0_64 = 0.0000004$. For some ***other solubilities,*** see page 146.

A
LABORATORY MANUAL
OF
QUALITATIVE ANALYSIS

The Century Chemistry Series
James Kendall, Editor

A LABORATORY MANUAL OF QUALITATIVE ANALYSIS

BY

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TO

R. W. M.

PREFACE

One feels the need of a decided reason for contributing another laboratory manual of qualitative analysis to the large number already extant. The author can offer no better reason than the fact that those who used his *Elementary Theory of Qualitative Analysis* liked it well enough to ask why a laboratory manual had not been written to accompany it.

In addition, it has been the hope of the author to find a more desirable procedure for the copper-tin group of metals than that involving separation by sodium or ammonium polysulphide. The precipitation of Group 2B from either of these two solvents is always confusing because of the simultaneous deposition of large amounts of free sulphur, which make it difficult to decide whether or not Group 2B sulphides are present, and often cause the student to make an analysis of the group when it is absent. Adapting the NaOH separation recommended by Böttger seems to overcome this difficulty without adding any other and more disturbing ones. Böttger rightly asserts that SnS is often not completely dissolved by NaOH, but if the tin is oxidized at the beginning of the group by HNO_3, little difficulty is encountered.

The author offers also his own arrangement of a systematic process for analysis of the so-called silver group of acid radicals (sulphides, ferrocyanides, ferricyanides, thiocyanates, chlorides, bromides, and iodides). It is hoped that in this procedure, the two bugbears, of separating ferrocyanides from ferricyanides and of separating chlorides from thiocyanates, bromides, and iodides, are overcome.

The procedures as written provide, in most cases, for the detection of 500 mg. of the element per 10 c.c., but it is recommended that not more than 250 mg. per 10 c.c. be used, and in most cases considerably less than this. In his own set of stock solutions, the author rarely uses as high as 100 mg. per 10 c.c., and usually the solutions range from 50 mg. per 10 c.c. down to 2 mg. The loss of time in filtering large precipitates and handling large bulks does not pay for the practice gained. With this particular view in mind, the quantities of reagents recommended in the manual are kept at a minimum.

The (flow) charts included to supplement the outline tables have been used with much success by the author and have been received with enthusiasm by the students. They are the same in principle as those recommended by Professor Hodge (*J. Chem. Ed.*, 6: 242 — Feb., 1927), but peculiarly enough, though the author has been using this type of chart since 1926, he was not aware of those of Professor Hodge until seeing them in Scott's *Qualitative Analysis*, in 1929.

The material in this text has been written to meet the needs of a complete course in elementary qualitative analysis, but, at the same time, the idea of a more abbreviated course has been kept in mind. By judicious omission of material, and without breaking the continuity seriously, this text may be readily adapted to a shorter course.

Thus, cadmium may be omitted at the end of Group 2A and the phosphate separation between Groups 2 and 3, without any break in continuity. By employing the bead tests for cobalt and nickel, in conjunction with the dimethylglyoxime test for both these elements, and by using the bead test for manganese and testing for iron on the combined hydroxide precipitate, the procedure for Group 3 may be decidedly simplified, with no change in order of procedure and no loss in accuracy. These alternative procedures are included in the notes and are not used as the preferred pro-

cedures simply because they do not give precipitation tests in all cases, and thus hinder the estimation of the amounts of the elements present. The test for strontium may be omitted in Group 4 without changing the procedure except to render the solution alkaline. In Group 5 the flame tests may be substituted for the precipitation tests for sodium and potassium.

In all, this gives a procedure for the metallic elements which lacks nothing in the accuracy usually attainable in qualitative analytical procedures and yet, by virtue of the sodium hydroxide procedure in Group 2 and the alternative tests suggested in Group 3, it is believed by the author to be as rapid if not more rapid than any of the accepted procedures of the standard texts.

For the matter of acid radicals, the sulphides, ferrocyanides, ferricyanides and thiocyanates may be omitted from the acids in Group 1 without change in the arrangement of material. The same is true for the tests for sulphites, oxalates and fluorides in the acid radicals in Group 2 and for the tests for the arsenates and arsenites in Group 3.

In arranging material the viewpoint of the teacher has been kept in the foreground at all times; therefore at each point where an explanation is involved, an encircled number calls attention to a note. To overcome the psychological tendency toward skipping material in fine print, all notes have been printed in full size type, set off by indentation and separated by asterisks. Wherever any reaction but the simplest is involved, the equation for that reaction is included in the notes. A digest of the principles of separation used in each group has been included at the end of the group, along with extended lists of questions of practical and theoretical nature, and equations.

In compiling this book, the author has felt particularly the influence of the excellent and exceedingly thorough text of Professor A. A. Noyes. This will be observed especially

in Groups 4 and 5 metals, in Group 2 acids, and in some of the notes. In the mind of the author, who has used Professor Noyes's text for eight years, no better procedures (considering brevity and simplicity) for these groups have been offered, and there was therefore no point in changing their general tenor.

The help of many other excellent texts on Qualitative Analysis and related subjects has been felt, consciously or otherwise. It would be difficult to mention the specific influences of each, but the author wishes particularly to acknowledge the help of the extensive work (in German) by Professor Böttger (1925 edition), of Treadwell-Hall, and Sears, whose book gave the suggestion upon which the analysis of the silver group of acid radicals is based.

The author wishes also to express his gratitude to Mr. Louis Koenig of New York University, for his willing cooperation, suggestions, and sacrifice of time in testing various procedures, and to Mr. Samuel Moskowitz for his helpful criticisms and reading of proof.

FREDERICK W. MILLER, JR.

New York, 1930.

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A
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A LABORATORY MANUAL OF QUALITATIVE ANALYSIS

INTRODUCTION

Qualitative analytical chemistry may be broadly defined as the process or processes of determining the separate parts, either elements or radicals, which make up an unknown chemical compound or mixture of chemical compounds, either in the dry form, in solution, or in suspension.

The aim is to determine what elements and radicals are present, and if possible, knowing the history or use of the substance, decide what chemical compounds composed the original material. Oftentimes it is not possible to go as far as this, because the processes of analysis determine only the presence or absence of individual ions. This is so because the analysis is conducted by dissolving the unknown substance in acids, or water if possible, and by subjecting this solution to treatment with a number of selected chemicals, called *reagents*. Since the properties of dissolved substances are characterized by the properties of the ions which they yield in solution, it is possible to establish the presence or absence only of the ions provided for in a given scheme of analysis.

Since the presence of ions only can be established, it is oftentimes difficult or impossible to tell of what compounds of these ions the original was composed. An example will make this clearer. Let us suppose we have a mixture from an industrial source, which contains sodium sulphate, zinc iodide, and barium chloride. This mixture may be dissolved

in water and analyzed by treating it with the various reagents, which characterize certain ions to the exclusion of others. We analyze on the one hand for metals (cations or basic constituents), and on the other hand for acid radicals or anions. The analysis would show that zinc, barium, and sodium were the cations present; sulphates, chlorides, and iodides, the anions. But unless the exact amount of each of these constituents were known, so that equivalent amounts of cation and anion might be sought and matched, the composition of the original could only be guessed at. A *quantitative* analysis, showing the exact amount of each radical present, would help to solve such a problem, but does not lie within the scope of qualitative analysis.

As will be seen later, the analysis for cations is a rather well-systematized eliminative process, based on the similarity of reaction of certain groups of metallic ions toward certain reagents. By means of certain so-called group reagents, the twenty-five common metallic radicals are subdivided into five groups. By means of other reagents, these groups are further subdivided, the process continuing until a reagent is added which characterizes only one cation. Unfortunately, the analysis for anions is not capable of as rigid a systematic treatment; but it can nevertheless be satisfactorily handled.

Successful execution of an analysis requires a thorough understanding of the principles involved, as well as the details of procedure. It is possible to carry out an analysis by merely following the directions without understanding them, but it is more often unsuccessful than not. It is rarely as successful as when the purpose and nature of each operation is thoroughly understood. Aside from this, the student should remember that the fundamental purpose of the course is not the development of technical skill in turning out an analysis which is accurate, but to illustrate certain important chemical principles and to teach a large number of chemical

facts in systematic, and therefore more easily remembered fashion. To become an analyst should hardly be the confessed goal of a chemistry student.

Therefore, so that the details of procedure may be understood, you must *read the notes* at the end of the procedures, and *understand* them, before proceeding to analyze a specimen. It is more important to remember what is contained in the notes than to remember the details of procedure, and it will be found that if the notes are thoroughly understood, the procedures are memorized with much less conscious effort. The necessity for understanding the underlying principles cannot be too emphatically stressed.

GENERAL NOTES ON PROCEDURE AND LABORATORY TECHNIQUE

Students frequently get the impression that since qualitative analysis is *qualitative* and not quantitative they need not be careful about complete transfer of precipitates, loss of small amounts of solution here and there, and other apparently small matters which really often make the difference between a clean, concise analysis and one which leaves the presence of some of the findings in doubt in the mind of the student. A good qualitative analysis should be semi-quantitative in nature, telling not only what is present but approximately how much. To do this properly the student must therefore minimize his losses. At certain points in the procedure small losses are almost unavoidable, yet this is the more reason for care at other points. Careful habits developed in qualitative work will more than repay the student in his subsequent quantitative work where scrupulous care is the first essential of acceptable results.

Some Common Errors. — One of the commonest errors on the part of students is to think that, because the bulk of a solution has been made large by the addition of water and other reagents, a part of the solution may be discarded in order to save time. The student forgets (more frequently never stops to think) that the total amount of each element originally present remains the same, regardless of what is added later and that each time he discards part of a solution, part of the original material is also being thrown away. Nothing can be more fatal to a successful analysis than two or three repetitions of this during the course of a complete procedure.

Another common error is to use only part of a large precipitate and discard the rest. Not only does this involve the same type of error, but it assumes that the precipitate is homogeneous. If it is a composite of more than one precipitate, it is probably not homogeneous because the different precipitates are more than likely to be of different densities, etc., and therefore settle with different degrees of rapidity. Any sample taken from a non-homogeneous mass will certainly not be representative and may even be totally lacking in one or more of the component precipitates.

It is with the hope of furthering careful manipulation and attention to details that the following instructions and precautions are set down.

General Orderliness. — The desk-top should be kept clean at all times, and the working materials arranged in orderly fashion. Care in such matters encourages care in chemical manipulations, and a neat-looking desk-top makes one feel more like working.

Pains should be taken to label accurately all solutions or precipitates which are not going to be used immediately. Hours of time are frequently saved by a few seconds spent in labeling things. A china-marking pencil which will "take" on glass, or the simple device of putting little slips of paper, properly marked, into the mouths of test-tubes, will be found satisfactory.

Reagents. — Reagent bottles should be kept clean. They frequently become soiled by evaporation of the solutions which they contain, by dust and other solids found in the air of the laboratory. There is always danger of contamination if such materials are not removed. It is a simple matter to rinse off each of the reagent bottles under the tap before beginning work.

After reagent bottles have been washed, they should be arranged in some systematic fashion in front of the student

on the shelf. They may be arranged in groups of acids, bases, and salts with each group alphabetized within itself. This saves a lot of time frequently wasted in hunting through a number of bottles for a desired reagent.

As a result of decomposition of the reagent itself or of the bottle which contains it, precipitates are often formed in the reagent bottles. They should be filtered as soon as this becomes evident. It is difficult to tell whether a precipitate is forming in a given test if one is being poured in from a reagent bottle.

When more has been poured than is necessary from a reagent bottle the excess should be thrown away. It should not be poured back into the reagent bottle. There is too much danger of contamination.

When the book recommends the use of a given quantity of a reagent, it should be measured in a small graduate rather than guessed at. The natural tendency is to use too much of a reagent when guessing. This results in loss of time in filtering unnecessarily large volumes of solution.

In all cases where the strength of the reagent is not specified it is to be understood that the dilute solution is to be used.

Evaporation of Solutions. — The process of evaporation of solutions is one frequently called for in the conduct of analytical processes. In all cases except those where the bulk is very large, such evaporations should be carried out in the following manner. Using a porcelain casserole and a flame not more than three inches in height, give the liquid a swirling motion in the dish by rotating the latter laterally in the flame. This spreads the liquid over a greater surface of the dish and thus exposes a greater surface of liquid, causing more rapid evaporation and at the same time preventing local superheating and bumping. This method may be employed (using a larger casserole) with volumes up to

FIGURE 1 A
Tearing Filter Paper

FIGURE 1 B
Insertion of Filter Paper in Funnel

100 c.c., which is as large as the usual run of procedure calls for. (On a clear day, with a good-sized dish and well-adjusted flame, the author has found that 100 c.c. may be evaporated to dryness in from five to seven minutes.)

When the procedure calls for evaporation to dryness, it is well when nearing the end of the evaporation to keep the dish above the flame rather than in it and to let the heat of the dish rather than the flame evaporate the last few drops. This prevents bumping and decomposition of the residue by overheating.

All evaporations of strong acids or strong ammonia, or ignition of residues which give off any kind of fumes, should of course be conducted under a well-ventilated hood.

It is frequently advisable to reduce the bulk of a solution even though the procedure may not call for it. Thus as a result of dilution with wash water, use of too large amounts of reagents, etc., the volume of the solution gets to a point where time is lost in filtering. A few minutes spent in evaporation may save a lot lost in filtering too large volumes. Care must be exercised, however, not to carry out such evaporations at points where the delicacy of the subsequent tests might be affected. If the student is in doubt he should always consult the instructor.

In general it may be said that for solutions containing not more than 10 mg. of an element per c.c., the total volume at any point in the procedure should not be allowed to go beyond 30 c.c. (a 6″ test-tube full) except when the procedure calls for more in a particular test. Failure to observe this is undoubtedly one of the largest causes of lost time in qualitative analysis.

Precipitation and Precipitates. — In the amounts of reagent recommended in the procedure, more has been called for than is actually equivalent to the elements or element in question. This is so because, by virtue of the common-ion

effect (see *Theory*, p. 102), the substance to be precipitated is rendered more insoluble by the addition of an excess of reagent. There is a distinct limit to this, however. It is a very natural tendency, if upon addition of the amount of reagent called for, no precipitate appears, to go on adding large quantities of the reagent in the hope of procuring a precipitate. This is useless and oftentimes harmful. Certainly it is a waste of reagent and time. As stated above, the amount of reagent to be added has been calculated, and if this amount does not bring the desired result, the trouble is to be sought elsewhere than in the addition of more reagent.

The procedure often calls for the addition of a reagent until no more precipitate forms. This may be determined in two ways. One is to allow the precipitate to settle until the liquid above is clear and then add another drop of reagent, carefully watching to see whether any more precipitate forms. If it does not, precipitation may be considered to be complete. If more forms, a little more of the reagent should be added and the test repeated. A more decisive way to make this test is to filter one or two c.c. of the solution and then add a drop or two of the reagent to the filtrate. This is often quicker and gives one a clear solution with which to work.

Precipitation with H_2S. — In the use of H_2S as a precipitating reagent, it is to be remembered that a slow stream, except in a few specific instances, serves just as well as a rapid one and contaminates the atmosphere less. The delivery tube for the H_2S should be of glass and should never be used unless it is spotlessly clean. Students are prone to neglect this and frequently find the traces of some previous solution in the one which they are analyzing. The delivery tube should be washed thoroughly inside and out immediately after each use. If washing the delivery tube does not

clean it, dip it into a test-tube half full of hot HNO_3. It is much more difficult to clean after the gelatinous precipitates have dried and the sulphides oxidized on its surface. Precipitation with H_2S should always be conducted in a flask or beaker rather than in a test-tube because a back pressure due to the depth of liquid in the latter slows up the passage of the gas and sometimes prevents such passage entirely.

To determine whether sufficient H_2S has been passed into the solution, remove the flask or beaker, blow away any gas that may be lying above the surface of the liquid, and test by holding a piece of filter paper, wet with $Pb(C_2H_3O_2)_2$, above the surface of the liquid (or simply by smelling). If the paper is blackened the liquid is saturated. Saturation is often indicated by the fact that the precipitate in the liquid settles well and leaves the liquid above it clear. Care exercised in this matter obviates confusion in subsequent groups because beginning students often get the impression that, if a sizable precipitate has formed, the precipitation is complete. This is by no means the case.

Filtration. — Certain precautions observed in the filtration of precipitates will facilitate their handling considerably. In the first place the funnel used should have a reasonably long stem (at least 4 inches) and should be so shaped that a filter paper folded in quarters fits snugly into it. Too obtuse or too acute an angle in the funnel will prevent proper fitting of the paper into the bowl of the funnel. The paper should be folded first into exact halves, then not quite into quarters and a triangular tab torn off in such a way as to leave a strip about one-quarter of an inch wide. (See Figure 1.) The folded paper is then opened into a hollow cone and inserted into the bowl of the funnel and filled with distilled water. While the water is running down the column of the funnel, the paper should be pressed against the walls of the funnel so as to exclude any air bubbles between the

walls and the paper and thus cause the snugly fitting paper to support a column of water in the stem of the funnel. This column of water, in addition to its capillary attraction for the liquid above, creates a gentle suction on the filter paper in trying to fall under the action of gravity. This speeds up the filtration appreciably.

Unless the directions specifically state otherwise, all liquids should be filtered while hot. Just as in the case of the well-known molasses, hot water is less viscous than cold and will run through a filter more rapidly.

The liquid to be filtered should be introduced onto the filter in small portions, guided to the filter paper by means of a glass rod (see Figure 2). This keeps the precipitate down near the point of the filter, making it easier to collect or transfer, and prevents the temptation to allow the liquid to rise above the top of the paper and thus permit the precipitate to run down outside the filter into the filtrate. Wherever possible the precipitate should be allowed to settle as much as possible before filtering, because the precipitate tends to clog the pores of the paper and thus inhibit rapid filtration.

If the precipitate tends to run through the paper because it is too finely divided, it should be digested (see next section) in the hot solution for a time and refiltered. Because of the enlargement of the particles of the precipitate by digestion and the fact that the pores of the paper have been somewhat clogged by adhering portions of the precipitate, the second filtration will often produce a clear filtrate. Further treatment of precipitates will be considered in the next section.

Wherever the use of suction filtration is available a great deal of time may be saved. A small suction flask (125 c.c.) is large enough for ordinary purposes. This should be fitted with a rubber stopper which holds an ordinary funnel and makes a tight joint. The paper should be fitted to the

FIGURE 2
Guiding Liquid and Precipitate to Filter

FIGURE 3
Washing Precipitate

funnel in the ordinary way but without any attempt to maintain the water column. A platinum or gold filter cone may be used to protect the paper, but with care, is not necessary. The suction should be applied gradually and very gently because the wet paper tears rather easily.

Treatment of Precipitates. — All precipitates should be thoroughly washed (see Figure 3) unless there are directions to the contrary. This is a notorious source of neglect. The student should keep in mind that a precipitate is always contaminated by adhering portions of the filtrate which may contain elements that would obscure certain tests on the precipitate. Thus if a precipitate which is to be tested for lead is not carefully washed to remove small amounts of barium in the filtrate, the latter, which is chemically similar to lead, may give light tests for lead when it is not present. The wash liquid should be hot wherever permissible and used in small successive portions rather than in one large one. It can be shown that these successive portions bring about more efficient washing. A precipitate may be considered to be completely washed when a small sample of the filtrate from the last washing shows the absence of some ion known to be in the original filtrate. Thus, if a given precipitate was formed in a solution known to contain a chloride, the precipitate should be washed with water until the filtrate no longer shows a precipitate with silver nitrate.

Many precipitates are thrown down in such finely divided form as to pass, at least partially, through the pores of the filter. This can be overcome by warming the solution containing the precipitate for several minutes. This process of digestion is known to increase the size of the particles of the precipitate. In some cases (colloidal sulphur, for example), digestion does not help particularly. Boiling the liquid with pieces of finely torn filter paper for several minutes and repeated filtration will be found distinctly helpful with such.

Economy in handling precipitates when they are being dissolved is an important feature of good technique. When dissolving a precipitate that has adhered somewhat to the walls of the vessel from which it was poured, the dissolving liquid should first be put into that vessel and then poured from it onto the precipitate. If the directions call for repeated pouring of the dissolving medium over the precipitate on the filter, the vessel from which the liquid containing some of the dissolved precipitate was last poured should be rinsed out with a small portion of fresh dissolving liquid and this used to wash any of the solution containing dissolved precipitate from the filter. The filter should then be lifted to allow the solution in the stem of the funnel to be united with the rest. Since precipitates in general are not very large and the amount of dissolving liquor recommended not very great, economy of the above nature is frequently important because loss of one c.c. of the solution containing the dissolved precipitate may represent from ten to twenty per cent of the whole.

Transfer of Precipitates. — Several methods for the transfer of a precipitate from a filter to a vessel, generally an evaporating dish, are available. For one, a hole may be punched through the filter with a glass rod drawn to a point and the precipitate washed into the receiving vessel by means of a stream from a wash bottle. After the precipitate has settled the water should be carefully decanted from the precipitate. Another method is to unfold the paper carefully, flatten it out on the side of the dish which is to receive the precipitate, and wash the latter into the dish by means of the wash bottle, decanting as before. Also, if the precipitate is not too large, the unfolded filter may be placed, precipitate side down, on the bottom of the dish and the extraneous liquid absorbed through the back of the filter by means of other dry filter paper, at the same time pressing the precipitate against the dish. The filter paper containing the

precipitate may then be peeled away, leaving practically all the precipitate in the dish. If this does not completely succeed on the first trial it should be repeated one or more times on a clean portion of the dish. Still another method is to stretch the unfolded filter on the bulged side of a watch glass laid on the desk and gently scrape the precipitate from the paper by means of a glass or horn spatula. The last adhering portions of the precipitate may then be washed into the dish by means of a wash bottle. All of the above methods entail some loss of precipitate, and if such a loss is undesirable by reason of the size of the precipitate, the paper and all should be transferred to the dish, the precipitate dissolved, and the paper then filtered away from the solution. Oftentimes the precipitate can be almost completely removed by holding one corner of the filter paper and sopping it up and down in the dissolving liquid (see Figure 4).

Beads and Wire Tests. — Before making any tests involving the use of platinum wire, the latter must be carefully cleaned. Too often some of the materials from a previous test give a slight color to the bead or flame which makes the test at hand doubtful and misleading. To clean the wire, it should be dipped in a few drops of concentrated hydrochloric acid poured on a watch glass (do not dip the wire in the reagent bottle) and heated in the flame. This should be repeated until no color is imparted to the flame.

For a bead test, the loop in the end of the wire may be made by wrapping the wire around the sharpened end of a pencil, thus obtaining a symmetrical loop about one eighth of an inch in diameter. The Na_2CO_3 or $Na_2B_4O_7$ should be prepared by holding the mouth of the reagent bottle near the flame and quickly inserting the hot loop of the wire so that the salt will adhere (see Figure 5). The bead is then heated in the flame until it is entirely melted

and symmetrically distributed on the loop. In making the actual bead test, the precipitate to be tested should be scraped up, a little bit at a time, and the bead then heated in the flame until no specks or particles are apparent in the molten bead in the flame. Using too much of the precipitate often makes a bead, which is supposed to be transparent, opaque, and thus obscures the test.

The student should remember that reactions between molten materials do not take place as rapidly as in ordinary solution. Patience should be the watchword in making bead tests. It is a good idea, sometimes, to lay the rod and wire on some supporting device such as the funnel stand, allowing the bead itself to be inserted in the proper part of the flame and to remain there for several minutes.

Record of Operations. — The record of observations and findings of an analysis of course depends largely on the discretion of the instructor. The keeping of a concise, promptly recorded set of notes is a difficult lesson to learn and yet is one that is absolutely essential to the conduct of worthwhile scientific work, particularly research. Consequently the student should form the habit of recording each step in the procedure for an analysis immediately after having made it. Not only is this habit correct, but notes made immediately after the event, when the student's impressions are fresh, form a more accurate record than notes made an hour or two later. The latter unfortunately are all too common among students.

A form of record which works very satisfactorily is illustrated in various instances in what follows (see page 40). This gives a consecutive and concise outline of what has been done and what has taken place. Several other methods of recording results are available and may be found to be equally satisfactory.

FIGURE 4
Removing Precipitate from Filter Paper

FIGURE 5
Preparation of Bead

PRELIMINARY EXPERIMENTS

Introductory. — *Qualitative Analysis* is a consecutively eliminative process, in which, by taking advantage, first, of the common properties of a group of radicals, then, perhaps, of a subgroup, and finally of the distinguishing property of a particular radical, the presence or absence of that radical is established. These eliminative processes are indicated in the group classifications below and in the preliminary experiments.

These experiments are presented to show the individual and distinguishing characteristics of the metallic ions, so that the student may witness the significant changes which a single element undergoes as it passes through the various processes of an analysis. The tests for the anions have been omitted because it is assumed that by the time the student reaches that part of the work, he will be sufficiently familiar with the operations and reactions of qualitative analysis to render such experiments unnecessary.

In performing these experiments, the student should keep a very close record of the color, nature, and solubility (in the various reagents recommended) of each precipitate formed and, by way of testing his knowledge of the properties of a given ion, should write the equations for each element given on pages 47 etc., after having seen the reactions take place.

It would obviously involve a too tedious and confusing task to show the effect of each reagent upon each element in a solution. Of necessity, many of the reagents added have no external effect upon a given radical in solution. When such a reagent is not involved in the immediate group of which the particular radical is a member, no mention is made of it and it may be assumed to have no major effect.

A statement of the groupings and group definitions of the ions to be sought will assist in the understanding of what is indicated in the previous paragraph. The metallic radicals sought are 25 in number (actually 22, since Pb is tested for in two places, as is Hg in its two valences; and NH_4 is not a metal), and are classified in five groups, as follows:

Group 1. — Pb, Ag, and Hg (monovalent): those metals whose chlorides are insoluble in water and dilute acid solution. The precipitating reagent is dilute HCl. The group is called the Chloride Group or Hydrochloric Acid Group. (Since $PbCl_2$ is somewhat soluble, Pb is not completely removed in Group 1, and therefore appears also in Group 2.)

Group 2. — Hg^{II}, Pb, Bi, Cu, Cd, As, Sb, and Sn: those metals whose chlorides are soluble in water and dilute acids, but whose sulphides are insoluble in dilute solutions of strong acids. They are precipitated by H_2S in HCl solution. This is called the Hydrogen Sulphide Group and is divided into two subgroups: (A), Hg^{II}, Pb, Bi, Cu, and Cd, those metals whose sulphides are not soluble in NaOH, and (B), As, Sb, and Sn, those metals whose sulphides are soluble in NaOH. The former is called the Copper and the latter the Tin Group.

Group 3. — Al, Cr, Fe, Co, Ni, Mn, and Zn: those metals whose sulphides are soluble in dilute solutions of strong acids but whose hydroxides and sulphides are insoluble in solutions made alkaline by NH_4OH, in the presence of ammonium salts. This is the so-called Ammonium Sulphide Group, since this compound is formed when H_2S is passed into NH_4OH, and causes the precipitation of the sulphides of the group.

Group 4. — Ba, Sr, Ca, and Mg: those metals which have soluble hydroxides and sulphides, but whose carbonates are insoluble in alkaline alcoholic solutions containing ammonium salts. This is the so-called Ammonium Carbonate or Alkaline Earth Group.

Group 5. — Na, K, and NH_4: those radicals whose chlorides, sulphides, carbonates, and hydroxides are soluble under the conditions laid down in the previous groups, and therefore remain in solution after the others have been precipitated. They have no common precipitating reagent and are called the Alkali or Soluble Group.

The Test Solutions. — The test solutions should be made up to contain 10 mg. ($\frac{1}{1000}$ of a gram) of each element or radical in each 1 c.c. of the solution. In this way the student will have an opportunity to see just how large a precipitate is formed in a given test and will thereby be enabled roughly to estimate the number of milligrams of a radical present in a given amount of his unknown solutions.

Before performing the experiments with the test solutions, the student should read carefully the procedures (beginning on page 43), and particularly the notes on the group in which he is interested, so that he may obtain data on what to expect, what compounds are formed, and what reactions take place in the preliminary experiments.

PRELIMINARY EXPERIMENTS ON THE GROUP 1 METALS

(*Hydrochloric Acid Group*)

Lead. — Dilute 2 c.c. of the test solution to 10 c.c. with H_2O and add dilute HCl drop by drop, shaking after each addition, until a precipitate begins to form. Allow this precipitate to settle, then add another drop of HCl. Is any further precipitation noticeable? Continue the addition of HCl drop by drop until no further precipitation takes place. Filter, dilute the solution to 50 c.c. and pass H_2S into it. Was the Pb completely precipitated by the HCl? Consult the table of solubilities in the Appendix (p. 218) and explain.

Perforate the filter paper containing the white precipitate of $PbCl_2$ and wash the precipitate into a test-tube with 10 c.c. of water. Boil this mixture and if the $PbCl_2$ does not

dissolve completely add more water. What can be said about the relative solubilities of $PbCl_2$ in hot and cold water? Allow the solution to cool and if any precipitate settles out, decant the liquid from it and discard the precipitate. Divide the liquid into two portions. To one portion add a few drops of dilute H_2SO_4 and shake. What is the precipitate? To the other portion add a few drops of HNO_3 and 2 c.c. of K_2CrO_4. What is the precipitate? Write all equations. Read Notes **1, 2, 5,** and **6,** pp. 45–46.

Silver. — Dilute 2 c.c. of the $AgNO_3$ test solution to 10 c.c. and add HCl until the white curdy precipitate no longer forms. Filter and pass H_2S into the filtrate. Is the Ag completely precipitated by HCl? What deduction can be drawn as the relative solubilities of $PbCl_2$ and AgCl? Compare them by consulting the solubility table on p. 218. Treat the AgCl with hot water in the same way as was done with $PbCl_2$. Is AgCl soluble in hot water? Suggest a method of separating $PbCl_2$ from AgCl. Decant the water from the AgCl and treat the latter with 5 c.c. of NH_4OH, shaking and warming slightly. Is the AgCl soluble in NH_4OH? To the solution of AgCl in NH_4OH, add HNO_3 until the solution is acid. What is the precipitate? Write the equations for the solution of AgCl in NH_4OH and its reprecipitation by HNO_3. Note that the addition of HNO_3 does not necessarily cause the precipitation of a nitrate. It is a common error for students to think that if a certain reagent is added a precipitate formed must necessarily contain one of the radicals of that reagent. Read Note **8,** p. 46.

Mercurous Mercury. — Dilute 2 c.c. of the test solution of $HgNO_3$ to 10 c.c. and add HCl until precipitation is complete. Filter and treat the filtrate with H_2S. Answer the same questions as for Pb and Ag. Treat the white precipitate of HgCl with hot water as above. Compare its solu-

bility with those of $PbCl_2$ and AgCl by referring to the table on p. 42. Can HgCl be separated from $PbCl_2$ in the same way as AgCl? Decant the water from the HgCl, add 5 c.c. of NH_4OH to the latter and warm. Filter the black precipitate and add HNO_3 to the filtrate. Does HgCl dissolve in NH_4OH? Is the black precipitate on the filter a single substance or a mixture of precipitates? To what is the black due? How could AgCl be separated from HgCl? Write equations for the reaction of HgCl with NH_4OH. Read Note **7**, p. 46.

PRELIMINARY EXPERIMENTS ON THE GROUP 2A METALS

(Copper Group)

Effect of HCl upon H_2S Precipitation. — To ½ c.c. of the test solution of $Cd(NO_3)_2$ in each of three test-tubes, add 1 c.c. of HCl in the first case, 3 c.c. HCl in the second, and 9 c.c. HCl third. Dilute each to 20 c.c. with water and pass H_2S into all of them for about two minutes. Is a precipitate formed in each case? What is the precipitate? Repeat the same experiments, using test solutions of $Hg(NO_3)_2$ and $Zn(NO_3)_2$. Compare the solubilities of the sulphides of these three metals in varying concentrations of HCl by arranging them in the form of a table. Read Note **3**, p. 55.

Mercuric Mercury. — To 2 c.c. of the test solution of $Hg(NO_3)_2$ add 1 c.c. of HCl and dilute to 10 c.c. Pass H_2S into the solution until precipitation is complete. Decant the liquid and wash the precipitate twice with hot water. Treat the precipitate with 2 c.c. of NaOH and shake for a minute or two. Is the HgS completely soluble in NaOH? Filter and treat the filtrate with 3 c.c. of NH_4Cl. Is the HgS at all soluble in NaOH? Wash the main bulk of the HgS on the filter with hot water, and transfer it to a

test-tube. Add 5 c.c. of dilute HNO_3 and boil for a minute. Decant 1 c.c. of the HNO_3 and add 1 c.c. of $SnCl_2$ to it. Is the HgS soluble in boiling HNO_3? To the rest of the HNO_3-HgS mixture add 2 c.c. of HCl and boil for two minutes. Is HgS soluble in aqua regia? Write the equation. Is solution complete? If not, what is the residue? Why is it black? Filter the mixture and add 1 c.c. of $SnCl_2$ to the filtrate, one drop at a time. What changes take place? Is there more than one precipitate formed? If so, what are they? Write the equations for the reactions which take place. Read Notes **2** to **9**, pp. 59–61.

Lead. — Dilute 2 c.c. of the test solution of $Pb(NO_3)_2$ to 10 c.c. and add a drop or two of HCl. (Why so small an amount?) Pass H_2S into this mixture until precipitation is complete. Filter and wash the precipitate with hot water containing a drop of HCl. Using a small portion of the precipitate, test its solubility in NaOH as under Hg. Is it soluble in NaOH? Transfer the remainder of the precipitate to a test-tube or casserole and warm it with 5 c.c. of HNO_3. Does the PbS dissolve? Does it dissolve completely? What is the residue? Write the equations for the reaction. How would you separate PbS from HgS? Filter the solution of $Pb(NO_3)_2$, and to the filtrate add NaOH drop by drop until the solution is just alkaline. Is any precipitate formed? What is it? Continue to add NaOH drop by drop, shaking on each addition. Does the precipitate remain undissolved? Account for what takes place. Write the equations for the reactions which took place. What are hydroxides such as $Pb(OH)_2$ called? Make the NaOH solution distinctly acid with $HC_2H_3O_2$ and add K_2CrO_4. Read Notes **2**, **10**, and **11**, pp. 59, 61–62.

Bismuth. — To 2 c.c. of the test solution of $Bi(NO_3)_3$ add 1 c.c. of HCl and dilute the solution to 10 c.c. Pass

H_2S into this solution until precipitation is complete. Filter and wash the precipitate. Discard the filtrate. As with the PbS, dissolve the precipitate of Bi_2S_3 in HNO_3 by boiling, and filter. Write the equation for the action of Bi_2S_3 and HNO_3. To the solution of $Bi(NO_3)_3$, add NaOH as under Pb. Does the precipitate of $Bi(OH)_3$ (or BiOOH) redissolve in excess of NaOH? How would you separate Bi from Pb? Filter the $Bi(OH)_3$ and wash it with water. Dissolve it by pouring warm HNO_3 over the filter. To the filtrate add NH_4OH until the solution is alkaline. What is the precipitate now? Filter and wash the precipitate; discard the filtrate. Prepare sodium stannite by adding NaOH in small portions to ½ c.c. of $SnCl_2$, until the precipitate first formed is redissolved. Does stannous Sn bear any resemblance to Pb? Write the reaction and compare it with that written for Pb. Pour the Na_2SnO_2 over the filter containing the $Bi(OH)_3$. What is the black residue? Write the reactions. Of what type of reaction is this an example? Read Notes **14** to **16**, p. 62.

Copper. — Add **1** c.c. of HCl to **2** c.c. of $Cu(NO_3)_2$ test solution and dilute the mixture to 10 c.c. Pass H_2S into the solution until the precipitation is complete. Filter, wash the precipitate as before, and discard the filtrate. Dissolve the precipitate in 5 c.c. of HNO_3 and filter. Treat the filtrate with NaOH as in the case of Bi. Filter and wash the precipitate. Discard the filtrate. Dissolve the precipitate in warm HNO_3 as with Bi, and make the solution strongly alkaline with NH_4OH. Is there any precipitate? Explain, and write the equation. Divide the blue solution into three portions. Pass H_2S into one of them. What is the black (or dark brown) precipitate? To the other portion of the blue solution add KCN (*Care!!* KCN is a particularly quick-acting, dangerous poison) until the blue color has entirely disappeared. Pass H_2S into this colorless solution. Is any

precipitate formed? Account for this. (Be careful in disposing of the solution containing the KCN. Pour it down a drain [preferably under a hood], and rinse it down with water.) Acidify the third portion with acetic acid (why is this necessary?) and add to the solution so obtained a few drops of $K_4Fe(CN)_6$. This is a more delicate test for Cu than the formation of the blue color, and may show a test for Cu when the solution with NH_4OH does not appear to be blue. Read Notes **17** and **18,** p. 63.

Cadmium. — Add 1 drop of HCl (why so small an amount?) to 2 c.c. of $Cd(NO_3)_2$ test solution and dilute the mixture to 10 c.c. Treat with H_2S, filter, wash, discard the filtrate, and dissolve the precipitate in HNO_3 as before. Treat the $Cd(NO_3)_2$ solution with NaOH (as under Cu), filter, discard the filtrate, wash the precipitate, and dissolve it in HNO_3. Make the solution strongly alkaline with NH_4OH. Is $Cd(OH)_2$ insoluble in excess of NH_4OH? Does it bear any resemblance to Cu in this respect. Divide the NH_4OH solution into three portions, and treat them as the three solutions of Cu were treated, adding 2 c.c. of KCN, since the solution is already colorless. Does KCN prevent the precipitation of CdS as it did CuS? Explain. (The white precipitate of $Cd_2Fe(CN)_6$ is covered up by the rose color of $Cu_2Fe(CN)_6$ when both are present.) Read Notes **17** and **18,** p. 63.

PRELIMINARY EXPERIMENTS ON GROUP 2B METALS

(*Tin Group*)

Precipitation of Arsenic from an Arsenate. — To 2 c.c. of a test solution of H_3AsO_4 add 1 c.c. of HCl and dilute the mixture to 10 c.c. Pass H_2S into this solution without heating, and note the speed of formation of any precipitate. To another 2 c.c. sample of H_3AsO_4, add 2 c.c. of concentrated

HCl; heat this mixture almost to boiling and pass H_2S into the hot solution. Explain the difference in results. (Read Note **4**, p. 56.)

After the As_2S_{3-5} has been completely precipitated in this latter test, dilute the solution with 10 c.c. of H_2O (strong HCl attacks the filter paper) and filter. Wash the precipitate with hot water containing a little NH_4Cl (why?). Transfer the precipitate to a dish and treat it with 5 c.c. of NaOH. Write the equation for what took place. How would you separate As from the metals of Group 2A? Acidify the NaOH solution with $HC_2H_3O_2$. What is the precipitate? Write the reaction. Filter and wash the precipitate with hot water containing a little NH_4Cl. Transfer this precipitate to a dish and treat it with 10 c.c. of a mixture of NH_4OH, NH_4Cl, and H_2O in the ratio of 1:2:1, stirring thoroughly for about five minutes, or until the precipitate is completely dissolved. Write the equation. Filter if necessary, and acidify the solution with $HC_2H_3O_2$. Filter and wash the precipitate with hot H_2O and a little NH_4NO_3. Transfer the precipitate to a dish and boil it with 5 c.c. of HNO_3 until nothing more dissolves. What is the residue? Write the equation for the action. Evaporate the solution almost to dryness, dilute with 5 c.c. of H_2O, and filter. Make the solution alkaline with NH_4OH and add 2 c.c. of magnesia-mixture ($Mg[NO_3]_2$, NH_4NO_3, and NH_4OH). If no precipitate forms, allow the mixture to stand for ten minutes. What is the white precipitate? Is it crystalline or flocculent? Write the equation for the reaction. Filter and wash the precipitate with a small quantity of H_2O. Mix 1 c.c. of $AgNO_3$ with 5 drops of $HC_2H_3O_2$ and pour this solution over the filter. What is the precipitate? This is the confirmatory test for As. Read Notes **1** to **8**, pp. 69–71.

Antimony. — Add 1 c.c. of HCl to 2 c.c. of a test solution of $SbCl_3$, dilute to 10 c.c. and pass H_2S into the solution,

after it has been heated, until precipitation is complete. Treat this precipitate with NaOH, $HC_2H_3O_2$, and then with NH_4OH, NH_4Cl, H_2O as was done in the case of As, following the same order of procedure. Write equations for any reactions which took place. How would you separate As from Sb? Filter (using suction) the Sb_2S_3 from the NH_4OH, NH_4Cl, H_2O mixture and wash it with a little H_2O and NH_4NO_3. Suck the precipitate as dry as possible, transfer, with the filter paper, to a large test-tube, and dissolve it in 5 c.c. of concentrated HCl, by warming in a water bath and stirring thoroughly for five to ten minutes. Filter from the disintegrated filter paper. Dilute the solution to 27 c.c., transfer it to a small Erlenmeyer flask and partly submerge this in a bath of gently boiling water. After the solution becomes hot, pass H_2S into it for about ten minutes. What is the precipitate? Filter and transfer the precipitate to an evaporating dish. Dissolve it in 5 c.c. of conc. HCl, dilute to 10 c.c., and filter. Evaporate the filtrate to 2 to 3 c.c., cool, and insert a bright piece of granulated Sn, allowing the mixture to stand for five minutes. What is the black deposit? Explain why it is formed. Pour off the HCl and wash the tin, with its deposit of Sb, with a little water. Prepare some NaOBr solution by adding NaOH, drop by drop, to saturated Br_2 water, until the latter is decolorized. Pour this solution over the Sb deposit and allow it to stand for a few moments. Does the deposit dissolve? This is the confirmatory test for Sb. If the deposit were As, it would be dissolved. Write the reaction. Read Notes **9** to **16**, pp. 71–72.

Tin. — Starting with 2 c.c. of $SnCl_4$ test solution, repeat all the experiments outlined under Sb to the point where the saturation of the solution diluted to 27 c.c., with H_2S, is complete. Why is the Sn not precipitated? Read Note **3**, p. 55. Evaporate this solution to about 10 c.c. and boil it with 1 to 2 g. of powdered Sb (or Fe nails) for two to

three minutes. Filter from the Sb and quickly add 2 c.c. of HCl and a few drops of $HgCl_2$ solution. What is the precipitate? Compare this with the test for Hg. Why does this precipitate not turn gray, usually? Read Notes **17** to **20**, pp. 72–73.

PRELIMINARY EXPERIMENTS ON THE PHOSPHATE SEPARATION

Detection of the Phosphate Radical. — Dilute 1 c.c. of the test solution of Na_2HPO_4 to 5 c.c. and add 3 c.c. of conc. HNO_3. To this solution add 5 c.c. of $(NH_4)_2MoO_4$ reagent, warm gently (do not boil), and allow the mixture to stand for five minutes. Write the formula for the yellow precipitate formed. Read Notes **2** and **3**, pp. 85–86.

Test for Iron. — Dilute 2 c.c. of the test solution of $Fe(NO_3)_3$ to 10 c.c. and boil it with a few drops of HNO_3 to insure that all the Fe is oxidized to the ferric condition. To this solution add 2 c.c. of $K_4Fe(CN)_6$. What is the precipitate? Write the equation. Why is $K_4Fe(CN)_6$ used instead of KCNS? Read Note **4**, p. 86.

The Phosphates in Acid and Alkaline Solutions. — To 1 c.c. of a test solution of $Ba(NO_3)_2$, add 4 c.c. of H_2O and make the solution alkaline. To this mixture, add Na_2HPO_4 until precipitation is complete. What is the precipitate? Acidify this mixture with $HC_2H_3O_2$, making it distinctly acid. What would happen if the solution were made alkaline with NH_4OH in testing for the Group 3 metals, if there were phosphates and Ba in the solution? The same facts hold for Ca, Sr, and Mg.

Acidify 1 c.c. of a test solution of $Fe(NO_3)_3$ with 2 c.c. of $HC_2H_3O_2$ and dilute the solution to 10 c.c.; to this solution add Na_2HPO_4 until precipitation is complete. How does the phosphate of Fe (ferric) differ from that of Ba? The same facts hold for the phosphates of Cr and Al. Suggest a

method for separating Fe, Cr, and Al from Ba, Sr, Ca, and Mg.

Repeat the above test for Ba with a test solution of $Zn(NO_3)_2$. How might Cr, Al, and Fe be separated from Zn? The same is true for Co, Ni, Mn, and ferrous Fe. Read Note **5**, p. 86.

The Basic Acetates. — To 2 c.c. of a test solution of $Fe(NO_3)_3$ mixed with 2 c.c. of a test solution of $Mn(NO_3)_2$ add 1 c.c. of $HC_2H_3O_2$ and 3 c.c. of a 50 per cent solution of $NH_4C_2H_3O_2$. Note the color of the solution; note also the fact that there is no precipitate. To what compound is the color due? Dilute the solution to 30 c.c. and boil it for two to three minutes. What is the precipitate? To what is its formation due? Write the reaction. Filter the mixture and note the fact that the filtrate is colorless. What does this indicate? Cr and Al may be removed from solution in the same way. Make the filtrate slightly alkaline with NH_4OH and pass H_2S into it for two to three minutes. The precipitate is MnS. How might Co, Ni, and Zn, which act similarly to Mn, be separated from Al, Cr, and Fe? Read Notes **5** to **8**, pp. 86–88.

PRELIMINARY EXPERIMENTS ON THE GROUP 3 METALS

(Iron Group)

Ferrous and Ferric Iron. — To 2 c.c. of a test solution of ferrous ammonium sulphate, add 2 c.c. of NH_4Cl, and dilute to 10 c.c. with water and make alkaline with NH_4OH. What does this test indicate concerning the insolubility of $Fe(OH)_2$? Pass H_2S into the solution for two to three minutes. What is the precipitate? Filter and wash the precipitate with hot H_2O. Transfer the precipitate, with the paper, to an evaporating dish and treat it with 10 c.c. of a mixture of 1 part HCl to 4 parts H_2O. Filter if necessary and boil the solution to remove H_2S (origin?). Add ½ c.c. of conc.

HNO_3 to this solution and boil for a minute or more. Cool and make alkaline with NH_4OH. What is the precipitate formed? What was the purpose of the HNO_3? Write the reaction. Pass H_2S into the mixture containing the red-brown precipitate, for two to three minutes. What is the black precipitate? Filter and treat with diluted HCl as above. Read Notes **1** and **9**, pp. 102, 105.

Cobalt and Nickel. — To 2 c.c. each of test solutions of $Co(NO_3)_2$ and $Ni(NO_3)_2$, add NH_4OH until the solutions are distinctly alkaline. Are the hydroxides of Co and Ni insoluble in NH_4OH solutions? Are they insoluble in water? (See solubility table on p. 217.) Explain the difference. Pass H_2S into the ammoniacal solutions until the precipitations are complete. Filter separately and wash the two precipitates with hot water containing a little $(NH_4)_2S$. Make a borax bead test on each of the precipitates. (See **Bead and Wire Tests**, p. 15, for directions.) What are the colors of the two individual beads? Write the equations. Now make a combined bead test by taking a little of each of the sulphides of Co and Ni on a fresh borax bead. Which color is the predominant one? Read Note **3**, p. 107. Transfer the precipitates to separate evaporating dishes and treat them with solutions of 10 c.c. cold diluted HCl (1 part HCl [dil.] to 4 parts of H_2O). Stir the precipitate for two to three minutes thoroughly with a glass rod so that it may have good contact with the HCl. Do CoS and NiS dissolve appreciably in cold dilute HCl? To see if they dissolve at all, filter, make the filtrate alkaline with NH_4OH, and pass in H_2S. Is there any evidence that CoS and NiS dissolved at all? Transfer the precipitates from the filters to separate evaporating dishes and add 6 c.c. of HCl and 2 c.c. of HNO_3 to each. Boil the mixtures until nothing more dissolves. What is the undissolved material? Write the equations. Filter and evaporate the solutions until they are just moist;

do not ignite. Add 5 c.c. of H_2O to each and warm to assist solution if the residue is not already dissolved. Make both solutions alkaline with NH_4OH and divide each into two portions. To one portion each of the $CoCl_2$ and $NiCl_2$ solutions add a few drops of dimethyl glyoxime. Suggest a method of separating Co from Ni. If the solution of cobalt dimethyl glyoxime is not brown, look down through the solution in a test-tube. This brown color is a sensitive test for Co. To the other two portions of $CoCl_2$ and $NiCl_2$ add 3 c.c. each of NH_4Cl and 5 c.c. of nitroso-beta-naphthol. This is another method for the separation of Co from Ni. Read Notes **1** to **7**, pp. 106–109.

Aluminum. — To 2 c.c. of a test solution of $Al(NO_3)_3$, add 5 c.c. of H_2O, and make it alkaline with NH_4OH. What is the color of $Al(OH)_3$? Note another characteristic of $Al(OH)_3$ — air bubbles retained. Pass H_2S into the solution containing the suspended $Al(OH)_3$. Does any change take place? Explain why the $Al(OH)_3$ is not converted to Al_2S_3. Filter the precipitate of $Al(OH)_3$ and wash it with hot water. Dissolve it in 10 c.c. of diluted HCl made as directed under **Cobalt** and **Nickel.** How would you separate Al from Co and Ni? To the solution of $AlCl_3$, add NaOH drop by drop until a precipitate of $Al(OH)_3$ remains. Now continue to add NaOH a little at a time. Explain and write the equations. Dilute this solution with 5 c.c. of H_2O and boil. Is any precipitate formed? To this solution containing $NaAlO_2$ add conc. HCl drop by drop until the solution is acid. Now make the solution alkaline with conc. NH_4OH, added a little at a time and cooling between additions. What is the precipitate? Why was the addition of HCl necessary? Write equations. Filter and wash the precipitate with hot water. Dissolve the precipitate by repeatedly pouring 3 c.c. (the same 3 c.c.) of hot HCl over the filter. To the filtrate so obtained add 3 c.c. of

$NH_4C_2H_3O_2$ and 3 c.c. of Aluminon reagent. Allow this mixture to stand for three to four minutes and then add NH_4OH containing 5 c.c. of $(NH_4)_2CO_3$ until the solution is alkaline. Read Notes **13** to **15,** pp. 90–91.

Chromium. — Using 2 c.c. of a test solution of $Cr(NO_3)_3$ repeat the tests called for under **Aluminum** to the point where the precipitate is formed and redissolved by NaOH. Dilute this solution with 5 c.c. of H_2O and boil. What is the precipitate? Account for the difference between $Al(OH)_3$ and $Cr(OH)_3$ in this respect. Filter the precipitate of $Cr(OH)_3$ and wash it with hot water. Transfer it to an evaporating dish and add ½ c.c. of Na_2O_2 and 5 c.c. of H_2O. Bring the solution to gentle boiling, and boil until all the oxygen has been removed. Pour the solution into a test-tube. What is its color? To what is the color due? Write the equations. Filter if necessary, acidify the filtrate with $HC_2H_3O_2$ and add 5 c.c. of $Pb(C_2H_3O_2)_2$. What is the precipitate? Read Notes **9** to **11,** pp. 88–89.

Manganese. — To 2 c.c. of a test solution of $Mn(NO_3)_2$, add 3 c.c. of NH_4Cl and make the solution just alkaline with NH_4OH. Dilute the solution to 10 c.c. Is $Mn(OH)_2$ insoluble in the presence of NH_4Cl? Is it insoluble in H_2O? Why does it not precipitate in this case? Pass H_2S into the solution until precipitation is complete. What is the color of MnS? Treat the precipitate with 10 c.c. of diluted HCl as under Co and Ni, etc. How would you separate Mn from Co and Ni? Boil this solution to remove H_2S, and add NaOH as was done in the case of Al and Cr. Is $Mn(OH)_2$ soluble in excess of NaOH? Why was the solution boiled before adding NaOH? If the precipitate of $Mn(OH)_2$ turns darker as it stands, explain why it does. Transfer the precipitate and solution to an evaporating dish, add ½ c.c. of Na_2O_2, and boil the mixture until all the oxygen is evolved. Explain the darkening of the precipitate. Is $MnO(OH)_2$

soluble in Na_2O_2? How would you separate Mn from Cr? Filter the precipitate and wash it with hot H_2O. Make a Na_2CO_3 bead test upon this precipitate as directed for the precipitate of MnS under (24) **Separation and Detection of Manganese,** p. 100. Dissolve the remainder of the $MnO(OH)_2$ by pouring 5 c.c. of hot HCl repeatedly (the same 5 c.c.) over the filter. Boil the solution thoroughly to remove any Cl_2. What is the source of Cl_2? To this solution add 3 c.c. of boiled NH_4Cl and make the solution alkaline with boiled NH_4OH. What is the purpose of boiling these solutions? How would you separate Mn from Fe? Read Notes **16** to **19,** pp. 110–111.

Zinc. — Dilute 2 c.c. of the test solution of $Zn(NO_3)_2$ with 6 c.c. of H_2O and make the solution alkaline with NH_4OH. Is there any precipitation? Look up the solubility of $Zn(OH)_2$ in water, p. 217, and explain the result just obtained. Pass H_2S into the solution until precipitation is complete. Filter, wash, and treat the precipitate with diluted HCl as under Co and Ni. How would you separate Zn from Co and Ni? Boil the $ZnCl_2$ solution to expel H_2S. Why? Repeat the addition of NaOH as under Al, and explain the results. To the solution add HCl and NH_4OH as directed under Al. How would you separate Al from Zn? Explain the basis for the difference. Pass H_2S into the ammoniacal solution until precipitation is complete, filter, and wash the precipitate with hot water. Make the confirmatory test given under (27) **Detection of Zinc,** p. 106. Read Notes **21** to **24,** pp. 111–112.

PRELIMINARY EXPERIMENTS ON THE GROUP 4 METALS

(*Alkaline Earth Group*)

Barium. — Dilute 2 c.c. of the test solution of $Ba(NO_3)_2$ with 5 c.c. of H_2O, and add 2 c.c. of $(NH_4)_2CO_3$ reagent. What is the precipitate? Add 7 c.c. of alcohol to the mix-

ture and note if there seems to be any further precipitation. Filter the precipitate and wash it with hot H_2O containing a little $(NH_4)_2CO_3$. Dissolve the precipitate by pouring 5 c.c. of hot $HC_2H_3O_2$ repeatedly (the same 5 c.c.) over the filter. Evaporate the solution to a volume of 1 c.c., add 3 c.c. of $NH_4C_2H_3O_2$ (why?) and 5 c.c. of H_2O. To this solution add K_2CrO_4 drop by drop, and warm. What is the precipitate? After precipitation is complete, add 5 c.c. of $HC_2H_3O_2$, shake thoroughly, and warm. Has the precipitate dissolved to any extent? Why is the solution of $BaCO_3$ in 5 c.c. of $HC_2H_3O_2$ evaporated to 1 c.c., and $NH_4C_2H_3O_2$ added? Read Notes **3** to **11,** pp. 123–125.

Strontium. — Using 2 c.c. of the test solution of $Sr(NO_3)_2$, repeat the experiments under **Barium,** excepting the last addition of $HC_2H_3O_2$. Is $SrCrO_4$ insoluble in weakly acid solution? How would you separate Ba from Sr? Add NH_4OH to the K_2CrO_4 solution until its color changes from orange to yellow, then add a 2 c.c. excess. Is there any precipitate? Now add 7 c.c. of alcohol, C_2H_5OH, and shake thoroughly. Is there any precipitate now? What is the precipitate? What is the purpose of adding the C_2H_5OH? What may be said about the solubility of $SrCrO_4$? Look it up in the table on p. 218, and compare it with the other chromates of this group. Perform the confirmatory test given in the last half of (30) **Detection of Strontium,** on the precipitate of $SrCrO_4$. Read Notes **13** to **19,** pp. 126–127.

Calcium. — Using 2 c.c. of the test solution of $Ca(NO_3)_2$, repeat the experiments done with $Sr(NO_3)_2$, excepting the confirmatory test. Is the chromate of Ca insoluble in weakly acid or alkaline alcoholic solutions? Compare its solubility with those of the other chromates of this group. To the alkaline alcoholic chromate solution add 3 c.c. of $(NH_4)_2C_2O_4$. Warm the mixture gently and allow it to stand until a precipitate forms. Filter and wash the pre-

cipitate of CaC_2O_4 with a little hot H_2O. Apply to it the confirmatory test for Ca given under **(31) Detection of Calcium.** Read Notes **20** to **22,** p. 127.

Magnesium. — Using 2 c.c. of the test solution of $Mg(NO_3)_2$, dilute it with 5 c.c. of H_2O, and add 2 c.c. of $(NH_4)_2CO_3$ reagent. Is the carbonate of Mg as insoluble in H_2O as those of Ba, Sr, and Ca? To the $(NH_4)_2CO_3$ solution, add 7 c.c. of C_2H_5OH and shake the mixture for ten minutes. What is the precipitate? Why must alcohol be added in the precipitation of this group? Filter this precipitate and apply the tests that were applied to the precipitate of $CaCO_3$, under **Calcium,** omitting the confirmatory test. Is the chromate of Mg insoluble in acid or alkaline alcoholic solutions? Compare its solubility with those of the other members of this group. Is the oxalate of Mg insoluble in alkaline solutions containing alcohol? Compare its solubility with that of CaC_2O_4 in the table, p. 218. To the $(NH_4)_2C_2O_4$ solution add 3 c.c. of conc. NH_4OH and 10 c.c. of Na_2HPO_4. Allow the mixture to stand for fifteen minutes unless a sizable precipitate forms sooner. What is this precipitate? Filter, and wash the precipitate with a little NH_4OH and H_2O. Apply the confirmatory test given in Note **25,** p. 134. Read Notes **24** and **25,** p. 128.

PRELIMINARY EXPERIMENTS ON THE GROUP 5 METALS

(Alkali Group)

Potassium. — To 2 c.c. of the test solution of KNO_3, add 8 c.c. of H_2O and 2 c.c. of $Na_3Co(NO_2)_6$. Let the mixture stand for fifteen minutes unless a precipitate forms sooner. Filter and wash the precipitate thoroughly with cold H_2O. Note the color of the precipitate. What is its formula? Pour a 5 c.c. portion of hot HCl over the precipitate on the filter until the precipitate is dissolved. Evaporate the solu-

tion to 1 c.c. and apply the flame test with a clean platinum wire, using a celluloid screen or cobalt glass thick enough to absorb any yellow light from the Na flame (source?). Note the color of the K flame and that it is only a flash.

Repeat the same tests with 2 c.c. of a test solution of NH_4NO_3. Why is the solution to be used for Na and K evaporated and ignited twice before performing the test for K? Does NH_4 show any flame color? Read Notes **1** and **7** to **12**, pp. 135, 136–137.

Sodium. — To 2 c.c. of the test solution of $NaNO_3$ add 3 c.c. of H_2O and an equal volume of KH_2SbO_4. Allow the mixture to stand for an extended period of time, overnight if convenient. Is the precipitate formed crystalline or flocculent? What is its formula? Does the precipitate seem to adhere to the sides of the tube? To test this, pour away the liquid and note whether the bulk of the precipitate adheres or not. Wash the precipitate with a little cold water and dissolve it by warming in 3 c.c. of HCl. Apply the flame test, using a clean platinum wire and no screen. What is the color of the Na flame? Is it just a flash, or is it sustained for a few seconds? Read Notes **2** and **12**, pp. 135, 137.

Ammonium. — Using 2 c.c. samples of the test solution of NH_4NO_3, perform the tests for NH_4 given under (**36**) **Detection of Ammonium.** Read Notes **13** to **16**, pp. 137–138.

PRELIMINARY EXPERIMENTS ON THE SEPARATIONS OF CATIONS INTO GROUPS

(Read the introductory discussion on pp. 1–5, and study the tables on pp. 38 and 41, and Charts 1 and 2 at the back of the book. Study the group definitions on pp. 18–19.)

Measure into each of 6 labeled flasks (125 c.c. capacity), 2 c.c. each of the test solutions of $AgNO_3$ (representing Group 1), $Cu(NO_3)_2$ (representing Group 2A), $SbCl_3$ (repre-

senting Group 2B), $Zn(NO_3)_2$ (representing Group 3), $Ba(NO_3)_2$ (representing Group 4), and $NaNO_3$ (representing Group 5). Number them 1, 2, 3, 4, 5, and 6 in the order in which they are named above. Add 2.5 c.c. of concentrated HCl to each, and dilute each to 10 c.c. with H_2O. In which of the six did a precipitate form? What is the precipitate? Explain its occurrence. Discard the mixture in flask 1, and dilute the solutions in the remaining flasks to 50 c.c. with H_2O. Pass H_2S into all of them for five minutes. In which does a precipitate form? What are the precipitates? Filter the mixtures in the two flasks containing the precipitates and discard the filtrates. Wash the precipitates with hot H_2O and transfer them to evaporating dishes (with the paper if necessary). Treat each with 5 c.c. of NaOH and stir the mixtures thoroughly with a glass rod. Which of the precipitates dissolves? Discard the CuS-NaOH mixture and acidify the NaOH solution containing the Sb_2S_3 with $HC_2H_3O_2$. Explain the result and discard the test. Remembering that the solutions in the remaining flasks (4, 5, and 6) are saturated with H_2S, make them alkaline with NH_4OH. Which gives a precipitate? What is the precipitate? Discard the mixture in this flask (4). Transfer the solutions in flasks 5 and 6 separately to casseroles and evaporate to a volume of 10 c.c. each; and if a precipitate of free sulphur (source?) forms in either, filter it, using filter paper pulp if necessary. (See **Treatment of Precipitates,** p. 13.) Add 8 c.c. of $(NH_4)_2CO_3$ and 10 c.c. of alcohol (C_2H_5OH) to each of the remaining solutions. In which is a precipitate formed? What is the precipitate? What conclusions can be drawn concerning the separations of the six groups and subgroups? Could Na be tested for in solution 6?

In one flask of the same size, mix 2 c.c. each of the same six test solutions and add 2.5 c.c. of concentrated HCl to the mixture. Filter from the precipitate of AgCl and discard the precipitate. Dilute the filtrate to 50 c.c. and pass

in H_2S until the solution is saturated (see **Precipitation with H_2S,** p. 10). Of what does the precipitate consist? Filter and wash the precipitate with H_2O. Transfer it to an evaporating dish (with the paper if necessary) and treat it with 5 c.c. of NaOH, stirring the mixture thoroughly. Is any change apparent? What has taken place? What is the residue? Filter and discard the precipitate of CuS. Acidify the NaOH filtrate with $HC_2H_3O_2$. What is the precipitate? Discard the test. Evaporate the 50 c.c. filtrate from the H_2S treatment to 10 c.c. and filter from any free sulphur. Make the solution alkaline with NH_4OH and saturate the solution with H_2S. What is the precipitate? Filter and discard the precipitate of ZnS. Boil the filtrate until it no longer smells of H_2S, and filter from any free sulphur. To the filtrate add 8 c.c. of $(NH_4)_2CO_3$ and 10 c.c. of alcohol, C_2H_5OH, and shake. What is the precipitate? Discard the precipitate. Evaporate the filtrate to a small bulk (3 c.c.) and, regardless of any precipitate which may have formed, make a flame test on the evaporated solution with a clean platinum wire. To what is the flame color due? Would it be advisable to test for ammonium salts on this filtrate, to see if they were present in the original solution? Explain your answer.

The experiments above have been carried out with an idea of indicating the main group separations, the reagents and general methods used in bringing about these separations. Each test solution contained a cation representing a particular group or subgroup, and the methods which isolated that particular cation would also serve to isolate the other members in the groups associated with that ion.

The following tables illustrate two methods of recording the operations just conducted. They are examples of more elaborate ones which will be given with each group and subgroup. They help to classify and memorize the facts of qualitative analysis, but after all, they are merely skeleton

Outline Table*

of

Preliminary Experiment on Group Separation

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Orig. sol.	HCl	White ppt.	Group 1 present	AgCl	Cu, Sb, Zn, Ba, and Na
2.	Sol. 1	H_2S	Col. ppt.	Group 2 present	Sb_2S_3, CuS	Zn, Ba, and Na
3.	Ppt. 2	NaOH	Partial solution	Group 2A present	CuS	Sb
4.	Sol. 2	NH_4OH H_2S	White ppt.	Group 3 present	ZnS	Ba and Na
5.	Sol. 4	$(NH_4)_2CO_3$, C_2H_5OH	White ppt.	Group 4 present	$BaCO_3$	Na

*See explanation on p. 39.

outlines and should *never* be used as substitutes for the detailed procedures in carrying out an analysis. These outlines tell nothing of the details which are frequently of paramount importance. For example, in analyzing for Fe, Mn, Cr, Al, etc., after having separated them from CoS and NiS with cold dilute HCl (see p. 98), it is absolutely essential to boil the solution before adding NaOH in the next step. Failure to do this will precipitate Zn out of place and render its detection quite unlikely. Yet the outlines for Group 3 merely indicate the addition of NaOH after having made the separation with HCl. The fault in the majority of inaccurate analyses can generally be traced to failure to pay attention to details.

*N.B. This is merely an outline to indicate the general way in which the operations performed in the analysis of a solution may be recorded, and, as will be noted in some of the tables later, is not as complete in some respects. Thus, in the column headed "Solution," only symbols for the elements remaining in the solution are set down. In later tables, an attempt is made to set down at least one formula for a compound of the metal in solution, though this frequently does not represent all the possibilities. Thus, a solution may contain several anions as well as several cations, e.g., in the solution obtained in line 1 above, there are the cations, Cu, Sb, Zn, and Ba, and the anions Cl and NO_3. It would be to no purpose to represent all the possibilities, so that in what follows, one set of anions is generally selected and the formulas with the cations written.

Concerning the method pursued in writing such a table as that above, it will be noted that when a precipitate is obtained by the addition of reagents, or operations performed in the line designated in the number column as 1, that precipitate thereafter is called Precipitate 1, and has nothing to do with whether that is the first precipitate or the fifth, or any other, precipitate formed in the course of the procedure. In other words, the number of the line in the table, and nothing else, determines the number of the precipitate in the table. The same rule holds for all solutions, residues,

etc. obtained and recorded. (This method of recording is the one recommended by W. A. Noyes in his *Qualitative Analysis* [Henry Holt, 1923 edition].)

It must be firmly kept in mind that, as stated before, this is merely an outline form to assist the student in systematizing his knowledge, and is totally lacking in details. It should, therefore, never be used as a guide in carrying out an analysis.

TABLE 1

Group Separations

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Prepared solution or orig. solution	HCl	White ppt.	Group 1 present	Chlorides of Ag, Pb, and Hg (see Table 2)	Groups 2, 3, 4, and 5
2.	Sol. 1	HNO_3,HCl, H_2S	Colored ppt.	Group 2 present	Sulphides of Hg, Pb, Bi, Cu, Cd, As, Sb, Sn (see Table 3)	Groups 3, 4, 5
3.	Ppt. 2	NaOH	Partial solution	Group 2A present	Sulphides of Hg, Pb, Bi, Cu, Cd (see Table 3)	Sulpho-salts of As, Sb, and Sn (see Tables 3–4)
4.	Sol. 2	NH_4OH, $(NH_4)_2S$	Colored ppt.	Group 3 present	Sulphides and Hydroxides of Co, Mn, Ni, Zn, Fe Cr, Al (see Table 6)	Groups 4 and 5
5.	Sol. 4	$(NH_4)_2CO_3$	White ppt.	Group 4 present	Carbonates of Ba, Sr, Ca, Mg (see Table 7)	Na, K, and NH_4 as chlorides, nitrates, and carbonates (see Table 8)

TABLE 2

GROUP 1 METALS

(*Hg* [*-ous*], *Ag*, *Pb*)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Orig. sol.	(NH_4OH) HCl	Wh. pt.	Group 1 present	$PbCl_2$, HgCl, AgCl	Groups 2, 3, 4, 5
2.	Ppt. 1	H_2O (hot)	Partial sol.	Hg and Ag prob. pres.	AgCl, HgCl	$PbCl_2$
3.	Sol. 2	HNO_3, K_2CrO_4	Yellow ppt.	Pb pres.	$PbCrO_4$	X
4.	Ppt. 2	NH_4OH	Black res.	Hg pres.	Hg, $HgNH_2Cl$	$Ag(NH_3)_2Cl$
5.	Sol. 4	HNO_3	White ppt.	Ag pres.	AgCl	X

PRECIPITATION AND ANALYSIS OF THE SILVER GROUP (GROUP 1)

(*Ag, Pb, Hg*[1])*

Definition. — Those metals whose chlorides are insoluble in water and dilute solutions of strong acids.

(1A) Preliminary Precipitation of the Group. — NOTE: In what follows, a test for each group is made on a small portion of the solution prepared for that group, to determine the presence or absence of it. In this way some rather lengthy procedures can be avoided; thus, if Group 2 is shown to be absent by the preliminary test, the evaporation of the main bulk to dryness, addition of 2.5 c.c. of HCl, saturation with H_2S, with probable dilution finally to 100 c.c. (and subsequent evaporation to 10 c.c.) may all be avoided. Of necessity, the conditions recommended in the preliminary tests are not such as to bring about complete precipitation of the group, since this is not desired, but merely to indicate the presence or absence of the group.

To 1 c.c. of the original solution (or an equivalent amount of solution of a solid dissolved according to the directions on p. 196 *et seq.*) add HCl 1 drop at a time until 1 c.c. has been added. Warm the mixture gently and let it stand a few minutes. A white precipitate indicates the presence of **Group 1.** Discard the test and treat the main bulk of the original solution by **(1).** If no precipitate is formed, pass directly to **(4A).**

(1) Group Precipitation. — To 10 c.c. of the original solution, which, if not already so, should be made nearly neutral

* For the sake of convenience in what follows the ions of the elements will be represented by their symbols alone, omitting their valence charges; i.e., the lead ion, Pb^{++}, will be represented merely as Pb. In cases where a distinction is necessary because of a multivalent element, this will be indicated either as -ous or -ic, or will carry a Roman numeral representing the valence.

with NH_4OH in a test-tube (if a precipitate [basic salt] forms in the still acid solution, add a drop or two of HNO_3 to dissolve it) — or to an equivalent amount of solution of a solid, dissolved according to the directions on p. 196 *et seq.* — add HCl drop by drop until no further precipitate forms. (Read the general notes on **Precipitation and Precipitates,** p. 9.) To prevent precipitation of BiOCl ③ and SbOCl, add 3 c.c. more of HCl ②. Filter, after allowing to stand three or four minutes, and wash the precipitate with 2 or 3 c.c. of cold HCl ④ diluted (1:10). (A white precipitate indicates the presence of the silver group. ①*) Treat the precipitate by (**2**) and the filtrate by (**4**).

(**2**) **Isolation and Detection of Lead.** — By means of a glass rod which has been drawn to a point, punch a hole in the filter containing the precipitate from (**1**) and wash the precipitate into a test-tube by means of small samples of hot water totaling not more than 7 to 10 c.c. After the precipitate has been completely washed into the test-tube, warm the mixture for two or three minutes to give the $PbCl_2$ an opportunity to dissolve ⑤. If solution is complete, Hg and Ag are absent. If a precipitate remains, filter it and wash it with a few c.c. of hot water. Treat it by (**3**) for Hg and Ag. To the filtrate containing the $PbCl_2$ add 2 c.c. of HNO_3 ⑥ and 2 c.c. of K_2CrO_4. A yellow precipitate indicates the presence of **Lead** and is $PbCrO_4$.

(**3**) **Separation and Detection of Silver and Mercury.**— Pour repeatedly over the paper containing the water-insoluble residue of (**2**), a 4 c.c. portion of conc. NH_4OH ⑧⑨. (A black residue ⑦ on the filter indicates the presence of

* The note covering the particular point will be indicated by a small encircled number, thus ① will refer to Note 1 at the end of the procedure. References to the companion volume of this manual, *Elementary Theory of Qualitative Analysis*, by the same author, are designated as follows: (See *Theory*, p. 117, etc.).

Mercurous Mercury.) Acidify the filtrate with HNO_3. (A white curdy precipitate of AgCl indicates the presence of **Silver.**) If much Hg^+ ⑩ is present and no test for Ag^+ is obtained, wash the black residue undissolved by NH_4OH, with a mixture of 4 c.c. of HCl and 5 c.c. of saturated Br_2 ⑪ solution, stirring the residue on the filter meanwhile. Wash and repeat the test for Ag on the residue now remaining on the filter, with NH_4OH and HNO_3.

NOTES ON THE PRECIPITATION AND ANALYSIS OF GROUP 1

1. Absence of a white precipitate for this group indicates complete absence of silver and monovalent mercury but not of lead because the chloride of the latter is much more soluble than the chlorides of the former two. This may be seen from the following data for the solubility of these chlorides in grams per liter at 18° C.

$$AgCl = 0.0015 \text{ g.}$$
$$HgCl = 0.0020 \text{ g.}$$
$$PbCl_2 = 14.35 \text{ g.}$$

Consequently lead must always be tested for in the following group where it is precipitated by H_2S, for if present in small quantity it may not be precipitated at all as chloride.

* * *

2. Though $PbCl_2$ is distinctly soluble, its solubility is greatly reduced by the common ion effect brought about by the excess of chloride ion introduced in adding HCl. (See *Theory*, p. 102.)

* * *

3. Excess of HCl also prevents the precipitation of Sb and Bi as SbOCl and BiOCl as a result of hydrolysis of the chlorides. This may be seen from the following equation:

$$SbCl_3 + HOH \rightleftarrows SbOCl + 2\,HCl.$$

This is an application of the Concentration Law (see *Theory*, p. 76 *et seq.*) and Hydrolysis. (See *Theory*, p. 129 *et seq.*)

4. HCl is used as the wash liquid for the group precipitate to prevent solution of the $PbCl_2$ and to prevent the precipitation of Sb and Bi. (See Notes **2** and **3**.)

* * *

5. The $PbCl_2$ is dissolved in a test-tube rather than directly from the filter paper because its slow solubility nearly always causes the latter method to be incomplete. It dissolves to the extent of 14.35 g. per liter at 18° C. and 26.22 g. per liter at 80°. Hence the use of hot water.

* * *

6. The solution of $PbCl_2$ is acidified with HNO_3 before making the chromate test for lead to prevent precipitation of small amounts of Ba if the original group precipitate has not been carefully washed.

* * *

7. The black residue in the test for Hg is a mixture of very finely divided free Hg and a white precipitate of $HgNH_2Cl$. These are formed as a result of auto-oxidation; those atoms of Hg which are reduced to the metallic condition causing the oxidation of whose which go to the mercuric condition, in forming the mercuric aminochloride. The equation for the reaction is:

$$Hg_2Cl_2 + 2NH_4OH \rightarrow HgNH_2Cl + Hg + NH_4Cl + 2H_2O.$$

* * *

8. AgCl dissolves in NH_4OH as a result of the formation of the weakly dissociated complex ion $Ag(NH_3)_2^+$. (See *Theory*, p. 165 *et seq.*)

* * *

9. If the $PbCl_2$ is not completely removed from the presence of AgCl and HgCl by hot water, treatment with NH_4OH for Ag may cause a turbid filtrate due to Pb(OH)Cl carried through. The latter is soluble in HNO_3, however, and does not affect the delicacy of the Ag test.

10. In the presence of much Hg, Ag, if present only in small amounts, may be retained on the filter paper and not be found in the filtrate. This is due to the fact that the free Hg probably reduces the AgCl to free Ag according to the reaction:

$$2AgCl + 2Hg \rightleftarrows 2Ag + Hg_2Cl_2$$

since Hg is above Ag in the electromotive series.

* * *

11. Br_2 converts Hg in the residue to $HgBr_2$ and the free Ag to AgBr. HCl dissolves the $HgNH_2Cl$ to form $HgCl_2$. $HgBr_2$ and $HgCl_2$ run through the filter, and the remaining AgBr is dissolved by NH_4OH.

SUMMARY OF GROUP 1

The principles of separation applied in this group, are:

1. (Of Group 1 from the remaining groups) that the chlorides of these metals are insoluble in dilute acid solution.

2. (Of Pb from Ag and Hg) that $PbCl_2$ is soluble in hot water.

3. (Of Ag from Hg[-ous]) that AgCl is soluble in NH_4OH.

Equations on Group 1 Metals

LEAD

1. Lead nitrate and dilute hydrochloric acid.
2. Lead chloride and hot water.
3. Lead chloride and potassium chromate.
4. Lead chloride and dilute sulphuric acid.

SILVER

1. Silver nitrate and hydrochloric acid.
2. Silver chloride and hot water.
3. Silver chloride and ammonium hydroxide.
4. Silver ammonia chloride and nitric acid.
5. Silver chloride and metallic mercury.
6. Silver and free bromine.

MERCURY (MONOVALENT)

1. Mercurous nitrate and dilute hydrochloric acid.
2. Mercurous chloride and hot water.
3. Mercurous chloride and ammonium hydroxide.
4. Metallic mercury and bromine.
5. Mercuric aminochloride and hydrochloric acid.

QUESTIONS ON GROUP 1 METALS

(See also *Theory*, pp. 168–174.)

1. Discuss the advantages and disadvantages of using HCl as the precipitating agent in Group 1 metals, instead of NH_4Cl. Could KCl or NaCl be used in place of the two mentioned?
2. If no precipitate is formed at the beginning of Group 1, may Pb be assumed to be absent?
3. Assume that a solution which contained the three elements of Group 1 was not treated for that group, but treated instead for Group 2. What would eventually happen to the Ag, Pb, and Hg(-ous)?
4. What would happen if, at the beginning of Group 1, a large excess of HCl were added? Is this in keeping with the Law of Mass Action? Explain.
5. In what other way might Pb be confirmed in the hot-water extract?
6. Explain the fact that the NH_4OH filtrate from the extraction of AgCl is sometimes turbid.
7. Why is the precipitate from NH_4OH treatment of HgCl black? What is the valence of Hg in the compound formed in this reaction? Account for the fact that Hg has apparently been both oxidized and reduced.
8. What is the effect on the Ag test of a great deal of Hg? What reactions take place? How is the difficulty overcome?
9. If the solution at the beginning of Group 1 were diluted with a lot of water, what errors might occur? Explain.
10. Why must Hg be tested for in two places as well as Pb?

TABLE 3

Group 2A Metals

(Hg [-ic], Pb, Bi, Cu, Cd)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Sol. 1 (Table 2)	HNO_3–evap. HCl, H_2S	Colored ppt.	Group 2 present	HgS, PbS, CuS, CdS, Bi_2S_3, As_2S_{3-5}, SnS_{1-2}, Sb_2S_{3-5}	Groups 3, 4, and 5
2.	Ppt. 1	NaOH	Partial solution	Group 2A present	HgS, PbS, CuS, CdS, Bi_2S_3	Na_3AsS_4, Na_3AsO_3S, etc., $NaSbS_2$, $NaSbSO$, etc., Na_2SnS_2O, Na_2SnSO (Na_2HgS_2)
3.	Ppt. 2	HNO_3	Partial solution	Hg prob. present	HgS, (S)	$Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$
4.	Ppt. 3	Aqua regia	Solution	X	(S)	$HgCl_2$
5.	Sol. 4	$SnCl_2$	White to gray ppt.	Hg pres.	$HgCl \rightarrow Hg$	X

TABLE 3 — *Continued*

GROUP 2A METALS

(*Hg* [*-ic*], *Pb*, *Bi*, *Cu*, *Cd*)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
6.	Sol. 3	NaOH excess	Flocculent ppt.	Bi, Cu, Cd prob. pres	$Bi(OH)_3$, $Cd(OH)_2$, $Cu(OH)_2$	Na_2PbO_2
7.	Sol. 6	$HC_2H_3O_2$ K_2CrO_4	Yellow ppt.	Pb pres.	$PbCrO_4$	X
8.	Ppt. 6	HNO_3 NH_4OH	White ppt. Blue col.	Bi prob. pres., Cu pres.	$Bi(OH)_3$, $BiOOH$	$Cu(NH_3)_4(OH)_2$, $Cd(NH_3)_4(OH)_2$
9.	Ppt. 8	Na_2SnO_2	Black res.	Bi pres.	Bi	X
10.	Sol. 8 (part)	$HC_2H_3O_2$, $K_4Fe(CN)_6$	Pink ppt.	Cu confirmed	$Cu_2Fe(CN)_6$, $(Cd_2Fe(CN)_6)$	X
11.	Sol. 8 (rest)	KCN, H_2S	Yellow ppt.	Cd pres.	CdS	X

PRECIPITATION AND SEPARATION OF THE COPPER AND TIN GROUPS (GROUPS 2A AND 2B)

[(A) Hg^{II}, *Pb*, *Bi*, *Cu*, *Cd*; (B) *As*, *Sb*, *Sn*]

Definition. — Those metals whose sulphides are insoluble in dilute solutions of strong acids (but whose chlorides, except Pb, are soluble).

(4A) Preliminary Precipitation of the Group. — Dilute 1 c.c. of the filtrate from (1) (or the original solution if Group I is absent) to 5 c.c. and pass H_2S into it for five minutes. A colored precipitate or yellowish turbidity (to be distinguished from free sulphur from oxidation of H_2S) indicates the presence of **Group 2.** Add the mixture to the main bulk of the filtrate from **(1)** and treat by **(4).** If no precipitate is formed pass directly to **(15).**

(4) Precipitation of the Copper and Tin Groups. — To the filtrate from the HCl precipitate **(1)** add 1 c.c. of conc. HNO_3 ① and evaporate the solution *carefully* to dryness ② (allowing the heat of the dish to evaporate the last few drops rather than the flame — *do not ignite*). To the residue in the dish add 2.5 c.c. of conc. HCl ③ and 5 ④ c.c. of H_2O. Transfer to a flask of 125 c.c. capacity and heat to boiling. Pass a rapid stream of H_2S into the hot solution for at least five minutes (or until the precipitate begins to collect in flocks and settle to the bottom). Without filtering, dilute to 40 c.c., warm to 70°, and pass in H_2S again until saturated. Filter 2 c.c. of the solution, dilute to 5 c.c., and pass H_2S into this clear solution for at least five minutes. If any precipitate forms, dilute the main bulk of the 40 c.c. solution to 100 c.c. and saturate with H_2S. Allow the pre-

cipitate ⑤ to settle thoroughly, and filter. Treat the filtrate ⑥ by (**15**) and the precipitate by (**5**).

(**5**) **Separation of the Copper and Tin Groups** ③. — Transfer the precipitate from (**4**) to an evaporating dish (without the filter paper if possible) ④ and treat it with 10 c.c. of 2*N* NaOH ①; warm slightly and agitate the precipitate with a glass rod. If the solution is complete the Cu group is absent. Filter. The filtrate may contain the elements of the Sn group and a small amount of Hg ②. To determine this add 2 c.c. of NH_4Cl to a small sample of the filtrate. If a small dark brown or black precipitate results, Hg is probably present. Treat the main bulk of the filtrate with 5 c.c. of NH_4Cl. Filter and unite the precipitate with the main bulk of the Cu group precipitate, above. Wash the combined precipitates with hot H_2O to which a few drops of NH_4NO_3 have been added ⑤.

The NaOH filtrate may contain As, Sb, and Sn. The combined precipitates may contain Cu, Pb, Bi, Cd, and Hg. Treat the former by (**11**) and the latter by (**6**).

ANALYSIS OF COPPER GROUP

(**6**) **Separation and Detection of Mercury.** — Transfer the precipitate ① remaining from the separation of the Cu and Sn groups, (**5**), to a casserole (with the paper if necessary). Boil and stir the precipitate thoroughly with 5–10 c.c. of HNO_3 ② for two to three minutes ③. (A few drops of $NaNO_2$ ⑤ will help the solvent action of the acid.) The undissolved residue may consist of free sulphur ④ and HgS ⑥, and the solution may contain Pb, Bi, Cu, and Cd as nitrates. Filter and treat the latter by (**7**). Wash the residue and then boil it with a mixture of HCl and HNO_3 ⑦ (in the proportion 3:1) until no further solution ⑨ takes place. Filter and discard the residue of free S. To the fil-

trate add $SnCl_2$ ⑧ drop by drop. A white precipitate turning gray indicates the presence of **Mercury** and is HgCl and Hg.

(7) **Separation and Detection of Lead.** — To the filtrate from (6) add NaOH ⑩ drop by drop until the solution is just alkaline. Then add a 4 c.c. excess and warm the solution gently ⑪ for a minute or more, and filter. The filtrate may contain Pb as Na_2PbO_2 and the precipitate may consist of the hydroxides of Cu, Bi, and Cd. Treat the precipitate by (8). To the filtrate containing the Pb, add $HC_2H_3O_2$ to acidity, and then add 2 c.c. of K_2CrO_4. A yellow precipitate indicates the presence of **Lead** and is $PbCrO_4$.

(8) **Detection of Copper.** — Wash the precipitate of the hydroxides of Cu, Bi, and Cd thoroughly with hot water and dissolve it in warm HNO_3. Add NH_4OH to the warm filtrate until it is distinctly alkaline, and warm for several minutes before filtering. A white precipitate may be $Bi(OH)_3$ ⑫. Treat it by (9). A blue filtrate indicates **Copper** and is due to the presence of the $Cu(NH_3)_4^{++}$ ion ⑬ ⑰. To confirm the Cu, acidify 1 c.c. of this filtrate with $HC_2H_3O_2$ and add a few drops of $K_4Fe(CN)_6$. A reddish color or pinkish red precipitate confirms Cu and is $Cu_2Fe(CN)_6$. A white precipitate may be $Cd_2Fe(CN)_6$, which is concealed by the red $Cu_2Fe(CN)_6$, if both are present. Treat the rest of the blue filtrate, which may contain Cd as the $Cd(NH_3)_4^{++}$ ion, by (10).

(9) **Confirmatory Test for Bismuth** ⑭. — Wash the white precipitate from (8), which may be $Bi(OH)_3$ and treat it on the filter with a 3 c.c. portion of sodium stannite (Na_2SnO_2) ⑮ prepared by adding NaOH to 1 c.c. of $SnCl_2$ until the white precipitate first formed completely redissolves. A black residue on the filter indicates the presence of **Bismuth** and is metallic Bi ⑯.

(10) **Detection of Cadmium.** — To the blue filtrate from (8) add KCN (*care!! KCN is a violent poison*) until the blue color ⑱ disappears. If the filtrate is colorless the KCN may be omitted. Pass H_2S into this colorless filtrate to saturation. A light yellow precipitate indicates **Cadmium** and is CdS. If the precipitate is not pure yellow, filter (*be careful in discarding the KCN filtrate!!*) and wash the precipitate thoroughly with water. Treat it then with 10 c.c. of a mixture of H_2SO_4 and H_2O (1:1) and boil for several minutes, dilute to 30 c.c. and saturate with H_2S. A pure yellow ⑲ precipitate is CdS. (See Note **18** for alternative procedure.)

NOTES ON THE PRECIPITATION OF THE COPPER AND TIN GROUPS

(*Groups 2A and 2B*)

1. The filtrate from Group 1 is treated with HNO_3 and boiled (during evaporation) to oxidize the As to the pentavalent condition, if it is not already present as such:

$$3AsCl_3 + 2HNO_3 + 8H_2O \rightarrow 3H_3AsO_4 + 2NO + 9HCl.$$

Since the solution contains chlorides added in Group 1, there will be $AsCl_3$ present. This compound is distinctly volatile at the boiling temperature of the solution and an appreciable amount, if not most, of the As may be lost in this way. H_3AsO_4 is not volatile. In addition, any divalent Sn is oxidized to the tetravalent condition:

$$3SnCl_2 + 2HNO_3 + 8H_2O \rightarrow 3H_4SnO_4 + 6HCl + 2NO.$$

This is desirable because the SnS_2, subsequently precipitated, is much more soluble in NaOH than SnS. In fact, SnS is seldom completely dissolved by the NaOH treatment.

* * *

2. The solution containing the HNO_3 is evaporated carefully to dryness to remove all acid present, and 2.5 c.c.

of conc. HCl added because the acid concentration is of fundamental importance in the proper precipitation of this group. 2.5 c.c. of conc. HCl when diluted to 100 c.c. give an acid concentration (about 0.3*N*) such that the most soluble of the Group 2 sulphides (CdS, SnS, PbS) will be completely precipitated but the most insoluble of the Group 3 sulphides (ZnS) will remain in solution, unless present in large quantities. (See *Theory*, p. 108.)

* * *

3. The precipitation of the Group 2 sulphides in acid solution depends upon the solubility product principle and the law of mass-action in the following way: At a given temperature, any solution saturated with H_2S, even though acid be present, has a definite concentration of the gas. This is ionized in two stages but only the ionization need be considered here:

$$H_2S \rightleftarrows 2H^+ + S^=$$

Since this is an equilibrium condition, the following equation must be satisfied:

$$[H^+]^2 \times [S^=] = K$$

It is apparent from this that the greater the concentration of the H^+ ion the smaller must be the concentration of the $S^=$ ion, and that the latter will decrease as the square of $[H^+]$. In other words, if $[H^+]$ is doubled, $[S^=]$ will be one fourth as great as before. The precipitation of a sulphide depends on three things: the concentration of the metallic ion M^{++} (assuming it divalent), the concentration of $S^=$, and the magnitude of the solubility product of the metallic sulphide in question. If the product of the former two exceeds the solubility product constant, i.e., $[M^{++}] \times [S^=] > K_{sp}$, the sulphide will be precipitated. (See *Theory*, p. 96 *et seq.*) The value of K_{sp} varies with the particular sulphide (assuming constant temperature). At a fixed temperature, K_{sp}, for each sulphide is a fixed value and, other things

being equal, is smaller as the sulphide is more insoluble. Thus, the order in which the sulphides are precipitated from solutions of increasing acid concentration in the cold is about as follows: As (both valences), Hg, Cu, Sb (both valences), Bi and Sn (tetravalent), Cd, Pb and Sn (divalent), Zn, Fe, Co, Ni, and Mn. Thus a solution which is of such acidity as easily to permit the precipitation of As would not precipitate Cd at all. For this reason (and others to follow) the solution containing 2.5 c.c. of HCl is finally diluted to 100 c.c. so that all of the Group 2, but none of the Group 3, metals may be precipitated as a result of the decrease in $[H^+]$ with dilution.

* * *

4. The solution containing 2.5 c.c. conc. HCl is first diluted with 5 c.c. of water and heated because As is precipitated rapidly under these conditions when it is in the pentavalent form. In a cold dilute solution of HCl, As in the pentavalent form is completely precipitated only after about twenty-four hours, whereas in hot concentrated solutions it is completely precipitated in five minutes. The reasons for this are several. In the first place, H_3AsO_4 is converted by H_2S to H_3AsO_3S and the latter is fairly stable in cold dilute solutions of HCl. It is rapidly decomposed on heating to H_3AsO_3, which in turn is rapidly converted to As_2S_3. In concentrated solutions of HCl the As is precipitated as As_2S_5 because of the increased concentration of the As^{+++++} ion resulting from the increased concentration of the H^+ ion in HCl, as is indicated by the equation:

$$H_3AsO_4 + 5HCl + H_2O \rightleftarrows AsCl_5 + 5H_2O$$
$$\Updownarrow$$
$$As^{+++++} + 5Cl^-$$

To summarize, in hot concentrated solutions of HCl, H_3AsO_3S is readily decomposed and at the same time more As^{+++++} ions are present by mass-action effect.

The solution is then diluted to 40 c.c., for in case Cd,

Pb, and Sn (divalent) be absent, the rest of the elements will be completely precipitated at this point and it will not be necessary to dilute to 100 c.c. The small sample of the filtrate is diluted in the ratio of 40:100 and saturated with H_2S to test for the presence of any Pb, Sn, and Cd which may not have been precipitated at the 40 c.c. concentration.

* * *

5. The colors of the sulphides of the Group 2 sulphides are as follows: Hg and Cu, black; Bi, dark brown; Cd, As^{+++++}, As^{+++}, Sn^{++++}, yellow; Sb (both valences), orange, and Sn^{++}, dark brown. Hg first precipitates as a white compound $HgCl_2.2HgS$, which later goes over to the black HgS. Helpful conclusions may often be drawn by observing the colors of the original precipitate of the group.

* * *

6. When members of this group are absent, a color change accompanied by a white precipitate of free S will often be observed. This is due to the oxidation, in acid solution, of H_2S by chromates, permanganates, ferric iron, etc. In the first case, there will be a change from orange to green, in the second from purple to colorless and in the last from yellow to colorless or light green. They are represented respectively by the following equations:

$$K_2Cr_2O_7 + 8HCl + 3H_2S \rightarrow 2CrCl_3 + 2KCl + 7H_2O + 3S$$
$$2KMnO_4 + 6HCl + 5H_2S \rightarrow 2MnCl_2 + 2KCl + 8H_2O + 5S.$$
$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S.$$

NOTES ON THE SEPARATION OF THE COPPER FROM THE TIN GROUP

(Groups 2A and 2B)

1. The separation of Group 2A (copper group) from Group 2B (tin group) depends on the solubility of the more acidic sulphides of the latter group in NaOH, according to the following equations:

$As_2S_3 + 6NaOH \rightarrow Na_3AsS_3 + Na_3AsO_3 + 3H_2O.$
$As_2S_5 + 6NaOH \rightarrow Na_3AsO_3S + Na_3AsS_4 + 3H_2O.$
$SnS + 2NaOH \rightarrow Na_2SnSO + H_2O.$ (This reaction is doubtful.)
$SnS_2 + 2NaOH \rightarrow Na_2SnS_2O + H_2O.$

The reactions for Sb are the same as those for As, except for Sb_2S_3, which yields the meta compounds (corresponding to a metaphosphorous acid HPO_2) instead of the orthophosphorous, H_3PO_3:

$$Sb_2S_3 + 2NaOH \rightarrow NaSbS_2 + NaSbSO + H_2O.$$

A help to remember the formulæ of these complex sulphides will be found in *Theory*, p. 138.
SnS is not readily soluble in NaOH and the mechanism of its solution is not clearly understood. For this reason Sn is oxidized to the higher valence in the first step of the group.

* * *

2. HgS is slightly soluble in NaOH solutions because it forms the complex $HgS_2^=$ ion with any sulphide ion present:

$$HgS + S^= \rightleftarrows HgS_2^=$$

This is particularly so with high concentrations of OH^- ion. The reaction is reversible and the HgS may therefore be reprecipitated by the addition of NH_4Cl, which, by virtue of the formation of weakly ionized NH_4OH, reduces the OH^- ion concentration. (See *Theory*, p. 111.)

* * *

3. The separation of the Cu from the Sn group may also be accomplished by use of sodium or ammonium polysulphides, Na_2S_x and $(NH_4)_2S_x$. In the former case, HgS is completely dissolved and must be analyzed for in the Sn group. In the latter case, the group division is the same as in the NaOH procedure. Both have certain disadvantages, chief among which is the fact that

upon acidification both polysulphides precipitate free sulphur in finely divided form according to the equation:

$$(Na \text{ or } NH_4)_2S_{(n+1)} + 2HCl \rightarrow 2(Na \text{ or } NH_4)Cl + H_2S + nS$$

and this makes difficult the detection of the flocculent precipitate of the Sn group. With the NaOH separation, no free sulphur is formed, and on the whole the separation is much cleaner and much less messy than either of the others. It is true that small amounts of HgS are dissolved, but this is easily reprecipitated by NH_4Cl and readily filtered.

* * *

4. It is best to remove the combined precipitates of the Cu and Sn groups from the paper before treating with NaOH because the latter causes the paper to disintegrate and swell, making the handling of the Cu group sulphides more difficult. (See General Notes, p. 14, for transfer of precipitates.)

* * *

5. The precipitate of the Cu group sulphides is washed with NH_4NO_3 to prevent the common tendency of amorphous precipitates, such as these sulphides are, from running through the filter in colloidal form. Colloids are either positively or negatively charged and the positive or negative charge of a strong electrolyte tends to neutralize the charge on the colloid and so cause its precipitation and coagulation.

NOTES ON THE ANALYSIS OF THE COPPER GROUP

1. This precipitate should be very carefully washed because of its tendency to dissolve in HNO_3 when chlorides are present (from HCl), because of the formation of aqua regia in which HgS is soluble. (See Note 8 below.)

* * *

2. The sulphides of Pb, Bi, Cu, and Cd dissolve readily in dilute HNO_3 according to the following equations:

$3MS + 8HNO_3 \rightarrow 3M(NO_3)_2 + 2NO + 4H_2O + 3S.$
$3MS + 14HNO_3 \rightarrow 3M(NO_3)_2 + 8NO + 3H_2SO_4 + 4H_2O.$

(The reaction for Bi is the same but balanced differently because it is trivalent.) HgS dissolves practically not at all unless the HNO_3 becomes too concentrated, and for this reason the solution should not be allowed to evaporate to any appreciable extent.

* * *

3. The solution in HNO_3 should not be heated for more than the two or three minutes recommended, because HgS tends to form a difficultly soluble sulphonitrate $2HgS.HgNO_3$ which is white in color. This in addition to the facts that the Hg may go into solution (see Note **1** above), and that PbS may be oxidized to $PbSO_4$ (which is insoluble), causing confusion in the Bi test.

* * *

4. The fact that a black residue is obtained after the HNO_3 treatment is not necessarily an indication of the presence of Hg, because the free S formed (see equations in Note **2**) melts and tends to enclose small amounts of the black or brown sulphides of the group. For this reason it is advisable to stir the precipitate thoroughly during the HNO_3 treatment.

* * *

5. $NaNO_2$ is recommended because the presence of HNO_2:

$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

helps the solvent action of HNO_3. The action is not clearly understood. It is a well-known fact that Cu metal will not dissolve in pure HNO_3 but dissolves readily in HNO_3 which contains traces of HNO_2.

* * *

6. In the presence of large amounts of HgS, CdS is incompletely dissolved by HNO_3. Therefore, if much Hg (large black residue) is present, a small sample of the solution in aqua regia should be tested for Hg and the

rest evaporated to dryness and gently ignited to volatilize the $HgCl_2$ formed by aqua regia. The residue is taken up in water, made ammoniacal with NH_4OH, filtered from any $Bi(OH)_3$ and tested with H_2S for Cd. This is not necessary unless there are unusually large amounts of HgS present.

* * *

7. HgS is not dissolved by HNO_3, probably because its sulphide ion concentration is so extremely low, on account of its great insolubility, that the HNO_3 does not oxidize the sulphide ion. Aqua regia is a much more powerful oxidizing agent and oxidizes the sulphide ion according to the following equation:

$$3HgS+6HCl+2HNO_3 \rightarrow 3HgCl_2 + 4H_2O + 2NO + 3S.$$

* * *

8. $SnCl_2$ reduces $HgCl_2$ to white HgCl, and if present in excess reduces the latter to free Hg. Hence the white precipitate turning gray:

$$2HgCl_2 + SnCl_2 \rightarrow 2HgCl + SnCl_4.$$
$$2HgCl + SnCl_2 \rightarrow 2Hg + SnCl_4.$$

* * *

9. The solution in aqua regia should be boiled to expel any free chlorine, because the latter may oxidize the $SnCl_2$ to $SnCl_4$ and so reduce its activity.

* * *

10. Advantage is taken of the amphoteric properties of $Pb(OH)_2$ in separating it from the hydroxides of Bi, Cu, and Cd, which are not appreciably amphoteric. (See *Theory*, p. 122, for discussion of amphoteric hydroxides.) The $Pb(OH)_2$ dissolves in excess of NaOH according to the equation:

$$Pb(OH)_2 + 2NaOH \rightarrow Na_2PbO_2 + 2H_2O.$$

This method of separation has the advantages over the usual H_2SO_4 separation of Pb, in that it avoids the objectionable, time-consuming evaporation of H_2SO_4, which

when hot and concentrated requires careful handling; in addition, $(BiO)_2SO_4$ is liable to be precipitated with the $PbSO_4$, and mistaken for it if the solution is allowed to stand.

* * *

11. The mixture is warmed only very gently because of the fact that $Bi(OH)_3$ is appreciably soluble in hot conc. NaOH. Under the above conditions, however, its solubility is quite negligible.

* * *

12. Bismuth is probably first precipitated in the form of $Bi(OH)_3$, which is unstable and loses water to form BiOOH. The Cu and Cd are precipitated as $Cu(OH)_2$ and $Cd(OH)_2$ respectively by simple metathesis.

* * *

13. The separation of Bi from Cu and Cd depends on the fact that the latter two form weakly ionized complex ions with NH_4OH and remain in solution whereas $Bi(OH)_3$ is precipitated. (See *Theory*, p. 133 *et seq.*)

* * *

14. The confirmatory test for Bi should always be made because hydroxides of the iron group may be precipitated here if the original group precipitate was not completely washed.

* * *

15. Sodium stannite is formed by adding excess of NaOH to $SnCl_2$ because the $Sn(OH)_2$ first precipitated is redissolved in the excess as a result of its amphoteric character. (See Note **11** on Pb.)

* * *

16. BiOOH and $Bi(OH)_3$ are instantly reduced by Na_2SnO_2 to free Bi, according to the equation:

$$2BiOOH\ (Bi[OH]_3 - H_2O) + 3Na_2SnO_2 \rightarrow 2Bi + 3Na_2SnO_3 + H_2O.$$

Other reducible substances such as $Fe(OH)_3$ and $Pb(OH)_2$ are not so quickly reduced in the cold as BiOOH and do not conflict.

17. A distinct blue color in the ammoniacal filtrate is sufficient evidence for the presence of Cu. The $Cu_2Fe(CN)_6$ is a more delicate test, however, and should be made whenever there is doubt of the blue color. A white precipitate is due to $Cd_2Fe(CN)_6$, but this will not obscure the pink of the Cu precipitate.

* * *

18. Cu and Cd both form complex ions with excess of KCN (see *Theory*, pp. 143–44); but the $Cu(CN)_3^=$ complex is so much more stable than the $Cd(CN)_4^=$ complex that the concentration of Cu ion is not great enough to permit the precipitation of CuS when there is even a very small excess of KCN. The Cd ion concentration under these conditions is still great enough to permit precipitation of CdS. This is by far the best means of separating Cu from Cd but is objectionable on account of the extremely poisonous character of KCN. The following alternative procedure is offered: To the main bulk of the blue filtrate for Cu and Cd, add H_2SO_4 until the solution is just acid, and then add 3 c.c. more, warm the solution gently and add about 2 gms. of pure iron powder, and shake the mixture for about two minutes. Filter 2 c.c., dilute to 5 c.c., and pass in H_2S until saturated. If a dark precipitate forms, Cu is not completely removed. Add an additional 1 gm. of iron powder and 2 c.c. of H_2SO_4 to the original bulk, and shake until the above test shows that Cu is completely removed. Filter the main bulk of the mixture, dilute with 20 c.c. of water, and saturate with H_2S immediately. A yellow precipitate indicates Cd.

In this procedure, advantage is taken of the fact that Fe has a much greater solution tension than Cu but only slightly greater than Cd, thereby displacing Cu ions from solution and forming Fe ions instead,

$$Fe + CuSO_4 \rightarrow FeSO_4 + \downarrow Cu,$$

but leaving the Cd undisturbed, since the concentration of the latter is rarely high enough to cause its precipitation.

The solution is treated with H_2S immediately to prevent oxidation of ferrous to ferric ion by air and a subsequent precipitation of H_2S to free S by the ferric ion, thus obscuring the yellow CdS.

* * *

19. In using the KCN separation of Cu and Cd, a black precipitate due to incompletely removed Pb and Hg sometimes results. If this happens, treat the precipitate, after washing, with 3 c.c. of dilute H_2SO_4 and 10 c.c. of H_2O. Boil the mixture thoroughly, filter, and dilute the filtrate to 40 c.c. Pass in H_2S. A yellow precipitate is CdS. HgS and CuS are not affected by dilute H_2SO_4, PbS is converted to insoluble $PbSO_4$, and CdS is dissolved, but reprecipitated from the more dilute solution.

TABLE 4

GROUP 2B METALS

(*As*, *Sb*, *Sn*)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Sol. 2 (Table 3)	$HC_2H_3O_2$	Colored ppt.	Group 2B present	As_2S_{3-5}, SnS_{1-2}, Sb_2S_{3-5}	X
2.	Ppt. 1	NH_4OH, H_2O, NH_4Cl	Partial solution	Sb, Sn prob. present	Sb_2S_{3-5}, SnS_{1-2}	$(NH_4)_3AsO_3S$, $(NH_4)AsS_4$, $(NH_4)_3AsS_3$, etc.
3.	Sol. 2	$HC_2H_3O_2$	Yellow ppt.	As prob. pres.	As_2S_{3-5}	X
4.	Ppt. 3	HNO_3, Mg mixture	White cryst. ppt.	As pres.	$MgNH_4AsO_4$	X
5.	Ppt. 4	$HC_2H_3O_2$, $AgNO_3$	Red ppt.	As conf.	Ag_3AsO_4	X
6.	Ppt. 2	Conc. HCl, H_2O, H_2S	Orange ppt.	Sb prob. pres.	Sb_2S_3	$SnCl_{2-4}$

TABLE 4—*Continued*

GROUP 2B METALS

(*As*, *Sb*, *Sn*)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
7.	Ppt. 6	Sn	Black dep.	Sb pres.	Sb	X
8.	Res. 7	NaOBr	No change	Sb conf.	Sb	X
9.	Sol. 6	Sb	X	Sn reduced	X	$SnCl_2$
10.	Sol. 9	$HgCl_2$	White ppt.→ gray	Sn pres.	$HgCl \rightarrow Hg$	X
11.	Ppt. 10	NH_4OH	Black ppt.	Sn conf.	$Hg\text{-}HgNH_2Cl$	X

ANALYSIS OF THE TIN GROUP (SUBGROUP 2B)

[*As, Sb, Sn*]

(11) Reprecipitation of the Group Sulphides. — To the NaOH filtrate from (**5**) containing the dissolved sulphides of As, Sb, and Sn, add $HC_2H_3O_2$ ①② in small portions until the solution is acid, and shake well to coagulate the precipitate on each addition. A flocculent precipitate which may be yellow, brown, or orange indicates the presence of the subgroup and may consist of As_2S_{3-5}, Sb_2S_{3-5}, SnS_{1-2}. Filter, wash with hot water containing a little NH_4NO_3, and treat by (**12**). Discard the filtrate and washings.

(12) Separation and Detection of Arsenic. — Treat the precipitate from (**11**), consisting of the sulphides of As, Sb, and Sn, with 15 c.c. of a mixture of 2 N, NH_4OH③, NH_4Cl, and H_2O in the ratio 1:2:1, and stir thoroughly for five to ten minutes. Filter, wash the precipitate with hot water and NH_4NO_3 as before, remove by suction as much liquid as possible, and treat by (**13**) for Sb. Acidify the filtrate with $HC_2H_3O_2$. A yellow flocculent precipitate indicates the presence of **Arsenic** and is As_2S_{3-5}. In doubtful cases ④, filter, wash with hot H_2O and NH_4NO_3, transfer to a dish, and dissolve the precipitate by boiling in 5 c.c. HNO_3. Evaporate almost to dryness, dilute with 5 c.c. H_2O, and filter. Make the solution alkaline with NH_4OH and add 2 c.c. of magnesia-mixture ⑤ ($Mg(NO_3)_2$, NH_4NO_3, and NH_4OH). Allow to stand for ten or more minutes, shaking occasionally ⑥. A white crystalline precipitate is $MgNH_4AsO_4$. Filter and wash with a minimum quantity of water ⑦. Mix 1 c.c. of $AgNO_3$ and 5 drops of $HC_2H_3O_2$

and pour it over the filter. A dark red residue on the filter confirms As and is Ag_3AsO_4 ⑧.

(13) Separation and Detection of Antimony. — Dissolve ⑨ the partially dried precipitate from **(12)** in exactly ⑩ 5 c.c. of concentrated HCl ⑨ by warming gently (slight evolution of gas only) ⑪ in a test-tube submerged in a bath of hot water for five minutes or so. Filter from any undissolved material (possibly As_2S_{3-5}) on a dry filter. Dilute the solution to just 27 ⑫ c.c. with H_2O. Transfer to a small Erlenmeyer flask and partly submerge this in a bath of gently boiling water. After the solution becomes hot, pass in H_2S for about ten minutes. A reddish orange precipitate, which may be Sb_2S_{3-5}, indicates the presence of **Antimony,** but should always be confirmed ⑬. To do this, filter while hot, and wash the precipitate with hot water. Treat the filtrate by **(14)** for Sn. Transfer the precipitate to a dish and dissolve it in 5 c.c. of conc. HCl. Add an equal volume of H_2O, filter and evaporate to 2–3 c.c. Cool and insert a bright piece of granulated Sn ⑭, allowing this mixture to stand for five minutes or longer. Carefully decant the liquid and wash the residue (chiefly on the Sn) with H_2O, by decantation. Treat ⑮ this residue with 2–3 c.c. of freshly prepared ⑯ NaOBr solution. (Add NaOH drop by drop to 1 or 2 c.c. of saturated Br_2 solution until this is decolorized; then add the same amount of NaOH again.) The black residue remaining confirms Sb and is metallic antimony.

(14) Detection of Tin. — Evaporate the filtrate from **(13)**, containing Sn, to about 10 c.c. and boil with 1–2 g. of powdered Sb ⑰ (or iron nails) for two to three minutes. Filter from the Sb and quickly ⑱ add 2–3 c.c. of HCl ⑲ and a few drops of $HgCl_2$ solution. A white precipitate ⑳ which may or may not turn gray indicates the presence of **Tin** and is HgCl or a mixture of HgCl and Hg. If this precipitate is doubtful, filter and wash it with warm H_2O.

Then pour NH_4OH over the filter containing the precipitate. A black color (see test for Hg [-ous] in Group 1) confirms Sn.

NOTES ON THE REPRECIPITATION AND ANALYSIS OF THE TIN GROUP

(*Group 2B*)

1. The sulphides of As, Sb, and Sn are precipitated from their sulpho salts (see Note **1**, p. 57) on acidification. The equations for As are as follows:

$$2Na_3AsS_4 + 6HC_2H_3O_2 \rightarrow As_2S_5 + 6NaC_2H_3O_2 + 3H_2S.$$
$$2Na_3AsO_3S + 6HC_2H_3O_2 + 3H_2S \rightarrow As_2S_5 + 6NaC_2H_3O_2 + 6H_2O.$$

These reactions are explained ionically on the basis of the formation of weakly ionized H_2S (see *Theory*, pp. 137–38). The equations for Sb and Sn are written in similar fashion.

* * *

2. A weak acid such as $HC_2H_3O_2$ is used because the sulphides of Sb and Sn are slightly soluble in a dilute solution of a stronger acid such as HCl. Small portions and vigorous shaking are recommended in order to get better coagulation and easier filtration of the precipitate.

* * *

3. $(NH_4)_2CO_3$ is often recommended for the separation of As from Sb and Sn. It is satisfactory when freshly prepared, but on long standing suffers hydrolysis and becomes increasingly strong in NH_4OH, thereby causing solution of appreciable quantities of Sb_2S_{3-5} and SnS_2. The reaction is:

$$(NH_4)_2CO_3 + 2HOH \rightarrow 2NH_4OH + H_2CO_3 \rightarrow H_2O + CO_2.$$

A mixture of $2N$ NH_4OH (this should be prepared with reasonable care), which is $1N$ with respect to NH_4Cl, is a much better solvent for the sulphides of As and dis-

solves so little of the sulphides of Sb and Sn that their consideration may be neglected. SnS_2 does dissolve to a very slight extent, but the milky turbidity which results on acidification would not be confused with the precipitation of As_2S_{3-5}. The reactions for the solution of the sulphides of As in NH_4OH are similar to those for solution in NaOH (see Note **1**, p. 57). The NH_4Cl reduces the alkalinity of NH_4OH by the common ion effect (see *Theory*, p. 112) and thus permits the solution of only the most acidic of the sulphides of the Sn group, namely those of As.

* * *

4. In event that the precipitate for As is not a pale lemon yellow the confirmatory test should be made. This depends on the conversion of the sulphides of As to H_3AsO_4 by oxidation with HNO_3. The equation for only one of the sulphides is given, the other being similar:

$$3As_2S_3 + 10HNO_3 + 4H_2O \rightarrow 6H_3AsO_4 + 10NO + 9S.$$

The H_3AsO_4 is then converted to $(NH_4)_3AsO_4$ by means of NH_4OH and precipitated as $MgNH_4AsO_4$ with the so-called "magnesia mixture."

* * *

5. "Magnesia mixture" is a mixture of the nitrates of Mg and NH_4 to which a little NH_4OH has been added to precipitate iron and other impurities in the salts. The NH_4NO_3 is added to prevent the precipitation of $Mg(OH)_2$ by NH_4OH (see *Theory*, p. 112).

* * *

6. On account of its tendency to form supersaturated solutions the mixture for precipitation of $MgNH_4AsO_4$ is allowed to stand for some time with shaking.

* * *

7. $MgNH_4AsO_4$ is appreciably soluble in water and should therefore be washed with a minimum quantity of the latter.

8. Ag_3AsO_4 is precipitated by addition of a soluble silver salt because it is more insoluble than $MgNH_4AsO_4$. $HC_2H_3O_2$ prevents the formation of the $Ag(NH_3)_2^+$ complex which would naturally hinder the precipitation of Ag_3AsO_4. (See *Theory*, p. 133.)

* * *

9. The sulphides of Sb and Sn are soluble in conc. HCl. The reactions are as follows:

$$Sb_2S_5 + 6HCl \rightarrow 2SbCl_3 + 3H_2S + 2S.$$
$$SnS_2 + 4HCl \rightarrow SnCl_4 + 2H_2S.$$
$$SnCl_4 + 2HCl \text{ (excess)} \rightarrow H_2SnCl_6.$$

The reactions for the two sulphides of lower valence are simple metatheses.

* * *

10. The directions for the amounts of reagents and manipulation at this point should be followed very carefully since the subsequent separation of Sb and Sn depend upon exact concentrations of reagents. For this reason excess H_2O is removed as far as possible by suction and an exact amount of HCl added.

* * *

11. If the bubbling (due to evolution of H_2S chiefly) is minimized, little As_2S_{3-5} will be dissolved in event that any was carried over from the previous separation. As_2S_5 is slightly soluble in conc. HCl, particularly when the latter is saturated with H_2S.

* * *

12. By carefully adjusting the amount of HCl and H_2O for the precipitation of Sb_2S_3, an H^+ ion concentration can be obtained which will permit the detection of small amounts of Sb in the presence of large amounts of Sn. This depends on the solubility products of the sulphides involved (see Note **3**, p. 55). If the solution is diluted or not kept hot, however, SnS_2 may be precipitated when a large quantity is present.

13. Since it is possible that other substances (e.g., As_2S_{3-5}, SnS_{1-2}) than Sb_2S_3 may be precipitated, the confirmatory test for Sb should always be made. It is first precipitated as sulphide so that its quantity may be better estimated.

* * *

14. Sn having a greater solution tension than Sb, will displace Sb ions from the solution in accordance with the electromotive series. A metal higher up in the series than Sn is not used since any Sn present would then be displaced.

* * *

15. As would also be deposited by Sn and for this reason NaOBr is used. This reagent dissolves As by oxidizing it to an arsenate:

$$2As + 5NaOBr + 6NaOH \rightarrow 2Na_3AsO_4 + 5NaBr + 3H_2O.$$

The Sb is not affected by NaOBr.

* * *

16. The NaOBr solution decomposes rapidly and therefore should be prepared just before using:

$$3NaOBr \rightarrow 2NaBr + NaBrO_3.$$

* * *

17. Powdered Sb is to be preferred to iron nails in the reduction of Sn from the stannic to the stannous condition, because the latter, on account of its position in the electromotive series, will deposit some metallic Sn from the solution. The reaction with Sb is as follows:

$$3SnCl_4 + 2Sb \rightarrow 3SnCl_2 + 2SbCl_3.$$

* * *

18. The solution is treated immediately because $SnCl_2$ is readily oxidized in the air to the stannic condition:

$$2SnCl_2 + 4HCl + O_2(air) \rightarrow 2SnCl_4 + 2H_2O.$$

19. HCl is added to prevent possible precipitation of SbOCl by hydrolysis:

$$SbCl_3 + 2HOH \rightleftarrows SbOCl + 2HCl.$$

* * *

20. The reaction for the detection of Sn is the same one used for confirming Hg, except that here the $HgCl_2$ is in excess and the $SnCl_2$ generally in small quantity, so that the HgCl is not so likely to be reduced to free Hg. (See Note 8, p. 61.)

SUMMARY OF GROUP 2

The principles of separation applied in this group, are:

1. (Of Group 2 from the remaining groups) that the sulphides of these metals are insoluble in dilute solutions of strong acids.

2. (Of Group 2A from Group 2B) that the sulphides of Group 2B are soluble in solutions of NaOH.

3. (Of Hg from Pb, Bi, Cu, and Cd) that HgS is insoluble in boiling solutions of dilute HNO_3.

4. (Of Pb from Bi, Cu, and Cd) that $Pb(OH)_2$ is amphoteric and therefore soluble in excess of NaOH.

5. (Of Bi from Cu and Cd) that $Bi(OH)_3$ is precipitated by NH_4OH.

6. (Of Cu from Cd) that CdS is precipitated from solutions containing excess KCN.

7. (Of As from Sb and Sn) that As_2S_{3-5} is soluble in dilute solutions of NH_4OH in the presence of NH_4 salts.

8. (Of Sb from Sn) that Sb_2S_3 is insoluble in fairly strong HCl solution of adjusted concentration.

Equations on Group 2A Metals

MERCURY (DIVALENT)

1. Mercuric nitrate and hydrogen sulphide.
2. Mercuric sulphide and sodium hydroxide.
3. Mercuric sulphide and dilute nitric acid.
4. Mercuric sulphide and aqua regia.
5. Mercuric chloride and stannous chloride (two reactions).

LEAD

1. Lead nitrate and hydrogen sulphide.
2. Lead sulphide and sodium hydroxide.
3. Lead sulphide and nitric acid.
4. Lead nitrate and sodium hydroxide in excess.
5. Sodium plumbite and acetic acid.
6. Lead acetate and potassium chromate.

BISMUTH

1. Bismuth nitrate and hydrogen sulphide.
2. Bismuth sulphide and sodium hydroxide.
3. Bismuth sulphide and nitric acid.
4. Bismuth nitrate and sodium hydroxide in excess.
5. Bismuth hydroxide and nitric acid.
6. Bismuth nitrate and ammonium hydroxide in excess.
7. Stannous chloride and sodium hydroxide in excess.
8. Bismuth hydroxide and sodium stannite.

COPPER

1. Copper nitrate and hydrogen sulphide.
2. Copper sulphide and sodium hydroxide.
3. Copper sulphide and nitric acid.
4. Copper nitrate and sodium hydroxide in excess.
5. Copper hydroxide and nitric acid.
6. Copper nitrate and ammonium hydroxide in excess.

7. Copper ammonia hydroxide and acetic acid.
8. Copper acetate and potassium ferrocyanide.
9. Copper ammonia hydroxide and potassium cyanide (two reactions).
10. Potassium cuprocyanide and hydrogen sulphide.

CADMIUM

1. Cadmium nitrate and hydrogen sulphide.
2. Cadmium sulphide and sodium hydroxide.
3. Cadmium sulphide and nitric acid.
4. Cadmium nitrate and sodium hydroxide in excess.
5. Cadmium hydroxide and nitric acid.
6. Cadmium nitrate and ammonium hydroxide in excess.
7. Cadmium ammonia hydroxide and acetic acid.
8. Cadmium acetate and potassium ferrocyanide.
9. Cadmium ammonia hydroxide and potassium cyanide.
10. Potassium cadmicyanide and hydrogen sulphide.

(Note that the equations for Cadmium are exactly parallel to those of Copper with the exception of the last two.)

Equations on Group 2B Metals

ARSENIC

1. Arsenious chloride and nitric acid.
2. Arsenic acid and hydrogen sulphide.
3. Arsenic sulphide and sodium hydroxide.
4. Arsenious sulphide and sodium hydroxide.
5. Sodium tetra-thioarsenate and acetic acid.
6. Sodium mono-thioarsenate, acetic acid, and hydrogen sulphide. (The H_2S comes from the simultaneous decomposition of the sodium tetra-thioarsenate.)
7. Sodium tri-thioarsenite and acetic acid.
8. Sodium arsenite and hydrogen sulphide (from the previous equation).

9. Arsenic sulphide and ammonium hydroxide.
10. Arsenious sulphide and ammonium hydroxide.
11. Ammonium tetra-thioarsenate and acetic acid.
12. Ammonium mono-thioarsenate, acetic acid, and hydrogen sulphide.
13. Ammonium tri-thioarsenite and acetic acid.
14. Ammonium arsenite and hydrogen sulphide.
15. Arsenic sulphide and nitric acid.
16. Arsenious sulphide and nitric acid.
17. Arsenic acid and ammonium hydroxide.
18. Ammonium arsenate and magnesium nitrate.
19. Magnesium ammonium arsenate and silver nitrate.

ANTIMONY

1. Antimony chloride and hydrogen sulphide.
2. Antimonous sulphide and sodium hydroxide.
3. Sodium meta-dithio-antimonite and acetic acid.
4. Sodium meta-monothio-antimonite and acetic acid.
5. Antimonous sulphide and ammonium hydroxide (dilute).
6. Antimonous sulphide and concentrated hydrochloric acid.
7. Antimonous chloride and hydrogen sulphide.
8. Antimonous sulphide and concentrated hydrochloric acid.
9. Antimonous chloride and metallic tin.
10. Sodium hydroxide and bromine water (two reactions).
11. Tin and sodium hypobromite.

TIN

1. Stannous chloride and nitric acid.
2. Stannic acid and hydrogen sulphide.
3. Stannous chloride and hydrogen sulphide.
4. Stannic sulphide and sodium hydroxide.
5. The reaction between stannous sulphide and sodium hydroxide is doubtful. It is therefore omitted.

6. Sodium di-thio-stannate, acetic acid, and hydrogen sulphide.
7. Stannic sulphide and ammonium hydroxide (dilute).
8. Stannic sulphide and concentrated hydrochloric acid.
9. Chlorostannic acid and hydrogen sulphide (dilution 27 c.c.)
10. Stannic chloride and metallic antimony.
11. Stannous chloride and mercuric chloride.
12. Mercurous chloride and ammonium hydroxide.

Questions on Group 2 Metals

(See also *Theory*, pp. 168–174.)

1. Why is HNO_3 added before evaporating the solution for Group 2?
2. Why is the solution for Group 2 evaporated to dryness?
3. Explain, in detail, the purpose of adding a definite amount of HCl and passing in H_2S at various dilutions in Group 2.
4. If the solution for precipitation of Group 2 with H_2S were diluted a great deal, what errors might occur?
5. In the precipitation of Group 2 with H_2S, the solution sometimes changes color, and a finely divided white precipitate is formed even when Group 2 is absent. To what sources might this be due? Write the equations.
6. What reactions take place when H_2S is passed into a cold dilute solution containing H_3AsO_4? Write the reactions.
7. Explain why As is more readily precipitated by H_2S in hot solutions which are strongly acid with HCl.
8. Is the concentration of H_2S higher when passed into a hot solution than when passed into a cold one? Why then is the procedure carried out in hot solution?
9. Give your explanation for the fact that the sulphides of Group 2A are insoluble in NaOH, whereas those of Group 2B are soluble.
10. Are any of the sulphides of Group 2A exceptional in this respect? Which? How is the difficulty overcome?
11. Why is HgS less soluble in NaOH which contains NH_4Cl?

12. Why is SnS_2 more soluble in NaOH than SnS? Would you expect As_2S_5 to be more soluble in NaOH than As_2S_3? Explain your answer.
13. Explain why HgS is not dissolved by boiling HNO_3, whereas the rest of the sulphides of Group 2A are. Why does HgS dissolve in aqua regia?
14. What would be the danger of boiling HgS with HNO_3 for too long a time? What effect might this boiling have upon the Pb test?
15. Why should the sulphides of Group 2A be very carefully washed before treatment with HNO_3?
16. A black residue often remains after treatment of the sulphides of Group 2A with HNO_3, but no test for Hg is obtained. Explain.
17. Why does the white precipitate which indicates the presence of Hg turn gray? Under what conditions would this not happen?
18. Suggest a method of determining that the white precipitate obtained in the test for Hg is really HgCl.
19. Why is the solution of HgS in aqua regia boiled thoroughly before $SnCl_2$ is added?
20. Upon what fact does the separation of Pb from the other metals of Group 2A depend? Name five other metals in the scheme of analysis which have this same property.
21. Why is the NaOH solution in which the hydroxides of Bi, Cu and Cd are suspended, not boiled vigorously?
22. Why is it always advisable to confirm the presence of Bi by means of Na_2SnO_2? How is this latter compound prepared? If $Pb(OH)_2$ were present along with $Bi(OH)_3$, would Na_2SnO_2 reduce it?
23. Upon what does the separation of Bi from Cu and Cd depend? Name other ions which are similar to Cu and Cd in this respect. Is advantage taken of this property in the latter cases?
24. Why is the confirmatory test for Cu made even though the NH_4OH does not appear to be blue?
25. Explain the function of KCN in the separation of Cu from Cd.
26. Suggest another method for the separation of Cu from Cd. What advantages has this method? Upon what theoretical principles does this method depend?

27. In separating Cu from Cd by means of iron, a dark precipitate is often obtained when H_2S is passed into the solution. What is this precipitate? How may this difficulty be remedied?
28. Explain the precipitation of the sulphides of Group 2B by means of $HC_2H_3O_2$ added to the NaOH solution.
29. What is the basis of the separation of As_2S_{3-5} from the sulphides of Sb and Sn? Why are NH_4Cl and H_2O added to the NH_4OH?
30. A faint yellow precipitate is sometimes obtained on acidifying the NH_4OH solution containing As, even when As is absent. Explain.
31. Suggest another method of separating As from Sb and Sn. What is the disadvantage of this method?
32. Describe and write the equations for the confirmatory test for As.
33. Explain the purpose of NH_4NO_3 in the so-called magnesia mixture.
34. Why is the solution from which $MgNH_4AsO_4$ is to precipitate allowed to stand for some time if a precipitate is not formed immediately?
35. What is the purpose of the $HC_2H_3O_2$ in the confirmatory test for As?
36. What is the Sb compound obtained by dissolving Sb_2S_5 in concentrated HCl? Account for the change in valence.
37. What is the basis of the separation of Sb from Sn? Why should directions be followed with particular care in this part of the procedure?
38. Why is not Zn used in the precipitation of free Sb? Upon what does the use of Sn for this purpose depend?
39. If As were accidentally carried over into the Sb test how would Sb be distinguished from it? Write the reactions which As would undergo.
40. Why should NaOBr always be freshly prepared? Write reactions.
41. Why is Sb to be preferred to Fe for the reduction of $SnCl_4$?
42. What is the purpose of HCl in the confirmatory test for Sn?
43. Why is the confirmatory test for Sn made immediately after the $SnCl_4$ is reduced to $SnCl_2$?
44. Could any other metals beside Sb be used for the reduction of $SnCl_4$ without precipitating nearly all of the Sn? What are they?

TABLE 5

PHOSPHATE SEPARATION

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Sol. 1 (Table 3) 1 c.c.	HNO_3, $(NH_4)_2MoO_4$	Yellow ppt.	Phosphate present.	$(NH_4)_3PO_4 . 12MoO_3$	X
2.	Sol. 1 (Table 3) 1 c.c.	HNO_3, $K_4Fe(CN)_6$	Blue ppt.	Fe pres.	$Fe_4(Fe[CN]_6)_3$	X
3.	Sol. 1 (Table 3) (rest)	HNO_3, NH_4OH, $HC_2H_3O_2$, $NH_4C_2H_3O_2$, $FeCl_3$, H_2O	Red-brown ppt.	PO_4 removed	$FePO_4$, $CrPO_4$, $AlPO_4$, $Fe(OH)_2C_2H_3O_2$, $Cr(OH)_2C_2H_3O_2$, $Al(OH)_2C_2H_3O_2$	$Co(NO_3)_2$, $Ni(NO_3)_2$, $Mn(NO_3)_2$, $Zn(NO_3)_2$, etc.
4.	Ppt. 3	H_2O, Na_2O_2	Yellow filtrate	Cr pres.	$Fe(OH)_3$	Na_3PO_4, $NaAlO_2$, $NaC_2H_3O_2$, Na_2CrO_4
5.	Sol. 4 3 c.c.	$HC_2H_3O_2$, $Pb(C_2H_3O_2)_2$	Yellow ppt.	Cr confirmed	$PbCrO_4$	X

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
6.	Sol. 4 (rest)	HCl, NH_4OH	White ppt.	Al pres.	$Al(OH)_3$	X
7.	Ppt. 4	HCl	Ppt. dissolved	X	X	$AlCl_3$
8.	Sol. 7	$NH_4C_2H_3O_2$, Aluminon, NH_4OH, $(NH_4)_2CO_3$	Red ppt.	Al conf.	$AlC_{22}H_{13}O_8$	X
9.	Sol. 3	NH_4OH, H_2S	Colored ppt.	Co, Mn, Ni, Zn pres.	CoS, NSi, MnS, and ZnS	Groups 4 and 5
10.	See Table 6 for the analysis of Ppt. 9.					

PRECIPITATION AND SEPARATION OF GROUP 3 WHEN PHOSPHATES ARE PRESENT

(15) Detection of Phosphate. — Evaporate the solution from (**4**) (or (**1**) if Group 2 is absent; in this case evaporation may not be necessary) to a volume of 10 c.c., and filter from any precipitate formed during the evaporation. If free sulphur ⑫ (formed by oxidation of H_2S) runs through the filter, boil the filtrate with small pieces of filter paper ⑫ torn up to give a pulp and filter again. One or two repetitions of this process generally suffice to give a clear filtrate. To 1 c.c. of this filtrate add 2 c.c. of conc. HNO_3. To this add 4 c.c. of a mixture of equal parts of $(NH_4)_2MoO_4$ and conc. HNO_3. Warm gently (do not boil under any circumstances) and allow to stand for at least ten minutes. A bright yellow precipitate indicates the presence of the **Phosphate** ② ③ radical and is $(NH_4)_3PO_4.12MoO_3$. Discard the mixture and proceed according to (**16**) for removal of phosphates ③. If phosphates are absent proceed with the main bulk of the above filtrate according to (**20A**) for the detection of the iron group (Group 3).

(16) Detection of Iron ④ when Phosphates are Present ④. — If phosphates have been found present, boil the main bulk of the solution obtained in (**15**), containing the phosphate radical (in addition to the elements of all the groups subsequent to Group 2), with 3–4 drops of conc. HNO_3 for two to three minutes, to insure oxidation of Fe to the ferric condition. To ½ c.c. of the solution so obtained add a few drops of $K_4Fe(CN)_6$. A deep blue precipitate indicates the presence of Fe and is $Fe_4(Fe[CN]_6)_3$.

Discard the mixture thus obtained and treat the main bulk of the solution obtained above by (17) for the removal of phosphates.

(17) **Removal of Phosphates** ⑤.— To the main bulk of the solution obtained in (16) after oxidation with HNO_3, add NH_4OH drop by drop until the solution is just alkaline, add $HC_2H_3O_2$ in the same manner until the solution is just acid, and then add a 4 c.c. excess. To this mixture add 3 c.c. of a 50 per cent solution of $NH_4C_2H_3O_2$ and then add $FeCl_3$ 1 c.c. at a time until the solution and precipitate formed have a rusty brownish red appearance (unless this condition already exists). Dilute this mixture to 60 c.c. with H_2O and boil in an Erlenmeyer flask until the precipitate which may consist of the phosphates and basic acetates of Fe, Cr, Al ⑥ begins to collect in flocks and settle readily (about three minutes), leaving a clear solution above when the flame is removed. Filter immediately ⑦ on a folded filter paper in a large funnel and wash the precipitate with hot water. Evaporate the filtrate to a volume of 10 c.c. in an open evaporating dish or beaker. Filter, discard any precipitate ⑧ and treat it in the ordinary manner for Group 3, by procedure (20), except that the tests for Fe, Al, and Cr are to be omitted. Transfer the large precipitate consisting of the phosphates and basic acetates of Fe, Cr, and Al to a casserole, add 10 c.c. of H_2O and 1 g. of Na_2O_2 in small portions with constant stirring ⑨. Boil the mixture until all evolution of O_2 has ceased, and filter ⑩. Discard the precipitate and treat the filtrate by (18) to detect Cr.

(18) **Detection of Chromium when Phosphates are Present.** — If the filtrate from (17) containing Al and Cr is a distinct light yellow in color, the presence of **Chromium** is indicated. The color is due to Na_2CrO_4. In case of doubt ⑪ acidify 3 c.c. of the filtrate with $HC_2H_3O_2$ and add 5 c.c. of

$Pb(C_2H_3O_2)_2$. A yellow precipitate confirms Cr and is $PbCrO_4$. Treat the main bulk of the yellow filtrate from (17) by (19) for the detection of Al.

(19) Detection of Aluminum when Phosphates are Present. — To the main bulk of the yellow filtrate from (18) add conc. HCl ⑫ ⑬ drop by drop (cool after each addition) until the solution is just acid, taking care to avoid any large excess. To this add conc. NH_4OH ⑬ until the solution is alkaline. A white flocculent precipitate which retains air bubbles and tends to float to the top of the solution indicates the presence of **Aluminum** and is $Al(OH)_3$, but should always be confirmed ⑭. To confirm, filter and wash the precipitate with H_2O, dissolve from the filter by pouring 3 c.c. of hot HCl repeatedly over it. To the filtrate so obtained, add 3 c.c. of $NH_4C_2H_3O_2$ and 3 c.c. of "Aluminon" ⑮ reagent. Allow this mixture to stand for three to four minutes and add NH_4OH containing 5 c.c. of $(NH_4)_2CO_3$ until the solution is alkaline. A bright red precipitate indicates the presence of Al.

An alternative ⑯ confirmation for Al, but one which must be very carefully carried out is as follows: Dissolve the $Al(OH)_3$ in 5 c.c. of HNO_3, add 5 c.c. of H_2O, 2–5 small drops (not more) of a 0.3*N* solution of $Co(NO_3)_2$ and make the solution just alkaline with NH_4OH. Filter with suction and wash the precipitate thoroughly, sucking as dry as possible after the last washing. Tear away those parts of the filter paper which do not contain any precipitate, roll the remainder into a small ball, and wind a spiral of platinum wire around this. Burn off the paper in the flame and ignite the residue for four to five minutes at a bright red heat. A blue residue, which is probably $Co(AlO_2)_2$, confirms Al.

NOTES ON THE PHOSPHATE SEPARATION

1a. During the evaporation of the solution to remove H_2S after the Group 2 precipitation and reduce the bulk to workable size, free sulphur may be formed as a result of the oxidation of H_2S by the oxygen of the air.

b. The fine fibers of the filter paper probably act as surfaces on which the colloidal particles of sulphur are deposited.

* * *

2. The phosphates of Ba, Sr, Ca, and Mg are insoluble in alkaline solution, and since the solution is made alkaline for the first time at the beginning of Group 3, there is danger that the alkaline earths may be precipitated out of place. For this reason phosphates must be tested for at the beginning of Group 3 and removed if they are present. They may be removed immediately, or left until later on in the analysis of Group 3. The latter procedure entails the precipitation of the alkaline earths with Group 3 and thus their possible subdivision if the amount of them present is less than equivalent to the amount of PO_4 present. Hence the author deems it more advisable to remove the phosphates immediately even though Al and Cr have to be tested for under somewhat disadvantageous conditions.

Oxalates, tartrates, silicates, borates, and fluorides also complicate the analysis of Group 3. The first two hinder the precipitation of Al, Cr, and Fe by virtue of complex ion formation. They are, however, to be taken care of in the preliminary procedure (see p. 197), being destroyed as organic material. The latter two interfere in the same way as do phosphates, but their compounds with the alkaline earths are sufficiently soluble for their precipitation to be restrained by the use of NH_4Cl. Silicates would ordinarily be detected during the preliminary treatment of the unknown and removed, if present, at that point.

3. The detection of the PO_4 radical depends upon the formation of the complex phosphomolybdate ion. To foster the formation of the latter, according to the following equation, large concentrations of HNO_3 and $(NH_4)_2MoO_4$ are added:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O.$$

The solution is warmed and not boiled because $(NH_4)_2MoO_4$ decomposes on boiling, to deposit MoO_3, which is yellowish white in color, and might be mistaken for the phosphomolybdate precipitate. This is a very sensitive test for the $PO_4^{\equiv}$ radical, as little as $\frac{1}{40}$ mg. being detectable.

* * *

4. Since the phosphate separation involves the addition of an iron salt, as will be seen later, the presence of Fe must be tested for before the phosphate separation is made. Since Fe is always in the ferrous condition after the removal of Group 2 (see Note 6, p. 57), it is oxidized to the ferric condition by HNO_3:

$$3FeCl_2 + 10HNO_3 \rightarrow 3Fe(NO_3)_3 + 6HCl + NO + 2H_2O.$$

Since strong HNO_3 oxidizes sulphocyanates and gives a momentary red coloration which might be mistaken for $Fe(CNS)_3$, the ferrocyanide test for Fe is used instead:

$$4Fe(NO_3)_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4(Fe(CN)_6)_3 + 12KNO_3.$$

* * *

5. The removal of the phosphate radical depends upon the fact that the phosphates of Fe, Cr, and Al are insoluble in weakly acid solutions, whereas the rest of the phosphates of the Group 3 metals and those of the alkaline earths are soluble under these conditions, especially if an excess of one of the trivalent metals is present. Therefore the solution is first made alkaline with NH_4OH to insure the removal of all strong acid, and then $HC_2H_3O_2$ is added to

turn the solution weakly acid. $NH_4C_2H_3O_2$ further reduces the acidity of the solution by common ion effect (see *Theory*, p. 102 *et seq.*) and later removes the excess of Fe. When the proper acidity of the solution is established, $FeCl_3$ is added in excess to insure the complete removal of the PO_4 radical and to prevent precipitation of the alkaline earth phosphates in the weakly acid solution:

$$FeCl_3 + Na_2HPO_4 + NH_4C_2H_3O_2 \rightarrow FePO_4 + HC_2H_3O_2 + 3NaCl.$$

Since $FePO_4$ has the lowest solubility product of all the phosphates concerned, its saturation value is reached first, and it is precipitated completely long before the saturation values of the other phosphates are reached. The $PO_4^{\equiv}$ radical being completely precipitated, the excess Fe now begins to combine with the $NH_4C_2H_3O_2$ to form red $Fe(C_2H_3O_2)_3$. Hence the instructions to add $FeCl_3$ until the brownish red color appears. The next step is to remove the excess Fe. This is accomplished by the hydrolysis (decomposition by water) of the $Fe(C_2H_3O_2)_3$ by addition of a large excess of H_2O, which by mass action effect tends to shift the equilibrium toward the formation of the insoluble basic-acetate:

$$Fe(C_2H_3O_2)_3 + 2HOH \rightleftarrows Fe(OH)_2C_2H_3O_2 + HC_2H_3O_2.$$

In addition, a higher concentration of the $Fe(OH)_2C_2H_3O_2$ (more complete precipitation) depends upon a greater concentration of the acetate ion and a smaller concentration of ionized $HC_2H_3O_2$. Both are fostered by a high concentration of $NH_4C_2H_3O_2$, hence the instructions to add 3 c.c. of a 50 per cent solution of the latter. Some free $HC_2H_3O_2$ must be left in the solution and an unduly large excess of $NH_4C_2H_3O_2$ must not be added, or there would be danger of precipitating the hydroxides of the bivalent elements of Group 3. Boiling helps the hydrolytic action and tends to coagulate the basic acetates which often remain in the state of colloidal precipitation.

6. It is to be remembered that all the reactions shown here by Fe are also shown to a lesser degree by Al and Cr, since the latter are usually present in smaller concentrations than Fe (after the $FeCl_3$ is added). Hence the final precipitate for the removal of phosphates consists of the phosphates and basic acetates of Fe, Cr, and Al. $FePO_4$ is yellowish white, $CrPO_4$ is green, and $AlPO_4$ is white. The corresponding basic acetates resemble their respective hydroxides in color.

* * *

7. The basic acetate of Cr will not be completely precipitated unless there is an excess of Fe present; this is another reason for excess $FeCl_3$. The hydrolysis of $Al(C_2H_3O_2)_3$ tends to be reversed on cooling. Therefore the solution is filtered immediately and while hot.

* * *

8. During the evaporation of the filtrate from the phosphate separation, some of the colloidally suspended basic acetates may be coagulated. These small amounts may be discarded.

* * *

9. Na_2O_2 gives a moderately vigorous evolution of oxygen when introduced into cold water in small portions. It may react with explosive violence when hot, therefore it should be added in small portions to a cold solution. It is well not to bring the Na_2O_2 into contact with paper because there is a natural tendency to thoughtlessly throw the paper containing some unused Na_2O_2 into the slop-jar. The moisture in the air or the water in the jar liberates oxygen with evolution of heat and fire often results. The Na_2O_2 is best transferred directly from the cans in which it comes, to the dish in which it is to be used, by means of spatula. If the gas is evolved steadily after the Na_2O_2 has been added and the mixture has been thoroughly stirred, it is evidence that sufficient peroxide has been added.

10. The reactions which take place upon addition of Na_2O_2 and H_2O are as follows:

(a) The basic acetates of Fe, Cr, and Al are first converted to hydroxides by the NaOH formed from Na_2O_2 and H_2O:

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

$$[Cr,Al,Fe](OH)_2C_2H_3O_2 + NaOH \rightarrow [Cr,Al,Fe](OH)_3 + NaC_2H_3O_2.$$

$$[Cr,Al,Fe]PO_4 + 2NaOH + H_2O \rightarrow [Cr,Al,Fe](OH)_3 + Na_2HPO_4.$$

(b) The hydroxides of Cr and Al are dissolved to form the soluble chromite and aluminate, because of their amphoteric character (see *Theory*, p. 122 *et seq.*), whereas the $Fe(OH)_3$, not being amphoteric, remains behind:

$$[Cr,Al](OH)_3 + NaOH \rightarrow Na[Cr,Al]O_2 + 2H_2O.$$

(c) The $NaCrO_2$ is then oxidized to yellow Na_2CrO_4 by the oxygen of the Na_2O_2:

$$3Na_2O_2 + 4H_2O + 2NaCrO_2 \rightarrow 2Na_2CrO_4 + 4NaOH + 2H_2O.$$

In this manner Cr, Al, and the $PO_4^{\equiv}$ pass into solution and leave the Fe behind.

* * *

11. The impurities in the Na_2O_2 frequently impart a brownish yellow to the solution which makes the yellow of Cr indecisive. In cases such as this, or where the yellow color is very weak, the confirmatory test is advisable. In addition, an estimate of the amount of Cr present may be made in this way. The confirmatory test must be made in acid solution to prevent the precipitation of $Pb(OH)_2$, but the acid must be a weak one, since $PbCrO_4$ is soluble in strong acids.

12. The solution is acidified with HCl because the HNO_2, often present in HNO_3, might cause reduction of the chromate to trivalent Cr. The solution is kept cool for the same reason. Cr would be precipitated as a grayish green hydroxide if present in the trivalent form and thus obscure the white $Al(OH)_3$.

* * *

13. Concentrated HCl and NH_4OH are recommended in the test for Al, to keep down the bulk, because the solution is likely to be rather strongly alkaline from the Na_2O_2. They must be added carefully, however, for three reasons: (a) considerable heat is generated when neutralization takes place in concentrated solutions; (b) too large excess of HCl will necessitate a large addition of NH_4OH and thus increase the bulk, and (c) too large an excess of NH_4OH will dissolve some of the amphoteric $Al(OH)_3$ to form NH_4AlO_2.

It is necessary to add HCl because NH_4OH will not precipitate $Al(OH)_3$ from the NaOH solution since the Al is present as part of the negative ion, AlO_2^-. The H^+ reverses the equilibrium shown below and permits the formation of the Al^{+++} ion, which may then be precipitated by the NH_4OH (see *Theory*, p. 127):

$$H_2O + H^+ + AlO_2^- \rightleftarrows Al^{+++} + \boxed{\begin{matrix} 3OH^- \\ H^+ \end{matrix}} + Cl^- \rightleftarrows HCl.$$

$$\Downarrow\Uparrow$$

$$H_2O$$

* * *

14. The confirmatory test for Al is always necessary unless the precipitate is large, because both NaOH (not used here but in a later test for Al) and Na_2O_2 frequently contain small amounts of Na_2SiO_3, which precipitates H_2SiO_3 when acidified. The latter looks very much like $Al(OH)_3$. In addition the glaze of the dish is likely to

be attacked by NaOH formed from Na_2O_2, to form Na_2SiO_3:

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O.$$

$$Na_2SiO_3 + 2HCl \rightarrow H_2SiO_3 + 2NaCl.$$

A small precipitate for Al should therefore always be looked upon with suspicion.

* * *

15. Aluminon is the commercial name for an organic compound called aurin tricarboxylic acid ($H_3C_{22}H_{13}O_8$), which gives a bright red precipitate of $AlC_{22}H_{13}O_8$.

* * *

16. The chemistry of the alternative confirmatory test for Al is not very well known but probably depends upon the formation of $Co(AlO_2)_2$, a blue compound. Care must be exercised not to use too much $Co(NO_3)_2$, because the black oxide of Co is liberated on ignition of the nitrate. This CoO might obscure the blue color of the test. In order to insure that the $Al(OH)_3$ shall contain no sodium salts, which would cause the ash of the filter paper to melt together, the Al is reprecipitated as $Al(OH)_3$.

SUMMARY OF THE PHOSPHATE SEPARATION

The principles of separation applied in this group are:

1. (Of separation of the phosphates) that the phosphates of Fe, Cr, and Al are insoluble in weakly acid solutions in the presence of NH_4 salts.

2. (Of excess Fe from the rest of Group 3) that the basic acetate of Fe is insoluble in diluted weakly acid solution.

3. (Of Cr and Al from the rest of Group 3) that the phosphates and basic acetates of Cr and Al are insoluble in diluted weakly acid solutions.

4. (Of Fe from Al and Cr) that $Fe(OH)_3$ is insoluble in the presence of Na_2O_2 and H_2O.

5. (Of Cr from Al) that $Cr(OH)_3$ cannot be precipitated from a solution of Na_2CrO_4 by NH_4OH.

Equations on the Phosphate Procedure

IRON

1. Phosphoric acid, ammonium molybdate and nitric acid.
2. Ferrous chloride and nitric acid.
3. Ferric nitrate and potassium ferrocyanide.
4. Ferric chloride and phosphoric acid.
5. Ferric chloride and ammonium acetate.
6. Ferric acetate and water (heated).

(Note: The reactions of chromium and aluminum in the phosphate procedure exactly parallel those of iron to this point (except oxidation by HNO_3) and are therefore not set down separately.

7. Ferric phosphate, sodium peroxide, and water.
8. Basic ferric acetate, sodium peroxide, and water.

CHROMIUM

1. Chromium phosphate, sodium peroxide, and water.
2. Sodium chromate and lead acetate.

ALUMINUM

1. Aluminum phosphate, sodium peroxide, and water.
2. Sodium aluminate and hydrochloric acid.
3. Aluminum chloride and ammonium hydroxide.
4. Aluminum hydroxide and hydrochloric acid.
5. Aluminum chloride and aluminon reagent. (No equation need be written, since the product is rather complex.)

Questions on the Phosphate Separation

(See also *Theory*, pp. 168–174.)

1. In what way does the presence of the phosphate radical complicate the procedure for the metals?
2. Why was the test for PO_4 not made at the beginning of Group 1 or 2? Could it have been made at either of these points?
3. Why must iron be tested for on the filtrate from Group 2 when the phosphate separation is being made?
4. Starting with the test for phosphates, give the name and purpose or purposes of each reagent added in connection with the phosphate separation, up to the point where water is added and the solution boiled. What is the purpose of the large dilution with H_2O?
5. What other acid radicals might cause complication of the metallic procedure? In what ways are they taken care of?
6. Define the term "hydrolysis," and explain in terms of theory its application in the phosphate separation.
7. Why is an excess of $FeCl_3$ added in the phosphate separation? Give two reasons.
8. What is the basis for the separation of Cr from Fe and Al?
9. Why is it advisable always to make the confirmatory tests for Cr and Al?
10. In the test for Al, the NaOH solution is acidified with HCl and then immediately made alkaline again with NH_4OH. Why is this necessary?
11. Why should the solution in the test for Al not be made too alkaline with NH_4OH?
12. What is the reason for the precaution of adding a very small quantity of $Co(NO_3)_2$ in the confirmatory test for Al?
13. What is the basis of the separation of Al from Cr?
14. If, before removing the phosphates, the filtrate for Group 3 were made alkaline with NH_4OH and no precipitate was obtained, would the phosphate separation be necessary? Explain.

TABLE 6

Group 3 Metals

(Fe, Cr, Al, Co, Ni, Mn, Zn)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Sol. 1 (Table 3) or Sol. 3 (Table 5)	HNO_3, NH_4Cl, NH_4OH, H_2S	Colored precipitate	Group 3 present	$Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, Fe_2S_3, CoS, NiS, MnS, and ZnS	Groups 4 and 5
2.	Ppt. 1	HCl (cold)	Partial solution	Co and Ni pres.	CoS, NiS	$FeCl_3$, $CrCl_3$, $AlCl_3$, $MnCl_2$, $ZnCl_2$
3.	Ppt. 2	Aqua regia	Solution	X	(S)	$CoCl_2$, $NiCl_2$
4.	Sol. 3 (part)	NH_4OH, DMG	Pink ppt. Brown sol.	Ni pres. Co pres.	NiDMG	CoDMG
5.	Sol. 3 (rest)	NH_4OH, NH_4Cl, NBN	Red ppt.	Co conf.	CoNBN	X

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
6.	Sol. 2	$NaOH$, H_2O, Boil	Colored ppt.	Fe, Mn, Cr present	$Fe(OH)_3$, $Mn(OH)_2$, $MnO(OH)_2$, $Cr(OH)_3$	$NaAlO_2$, Na_2ZnO_2
7.	Ppt. 6	H_2O, Na_2O_2	Yellow filtrate	Cr present	$Fe(OH)_3$, $MnO(OH)_2$	Na_2CrO_4
8.	Sol. 7	$HC_2H_3O_2$, $Pb(C_2H_3O_2)_2$	Yellow ppt.	Cr conf.	$PbCrO_4$	X
9.	Ppt. 7	HCl	Solution	X	X	$MnCl_2$, $FeCl_3$
10.	Sol. 9	NH_4Cl, NH_4OH	Red-brown ppt.	Fe pres.	$Fe(OH)_3$	$MnCl_2$
11.	Ppt. 10	HCl, $K_4Fe(CN)_6$	Blue ppt.	Fe conf.	$Fe_4(Fe(CN)_6)_3$	X

TABLE 6 — *Continued*

GROUP 3 METALS

(*Fe, Cr, Al, Co, Ni, Mn, Zn*)

12.	Sol. 10	H_2S	Pink ppt.	Mn pres.	MnS	X
13.	Ppt. 12	Na_2CO_3, $KClO_3$	Green bead	Mn conf.	Na_2MnO_4	X
14.	Sol. 6	HCl, NH_4OH	White ppt.	Al pres.	$Al(OH)_3$	$Zn(NH_3)_4(OH)_2$
15.	Ppt. 14	$NH_4C_2H_3O_2$, Aluminon, NH_4OH, $(NH_4)_2CO_3$	Red ppt.	Al conf.	$AlC_{22}H_{13}O_8$	X
16.	Sol. 14	H_2S	White ppt.	Zn pres.	ZnS	X
17.	Ppt. 16	HNO_3, $Co(NO_3)_2$, Na_2CO_3	Green res.	Zn conf.	$CoZnO_2$	X

PRECIPITATION OF THE IRON GROUP (GROUP 3)

($Fe^{II\,\&\,III}$, *Cr, Al, Co, Ni, Mn, Zn*)

Definition. — Those metals whose sulphides and hydroxides are insoluble in solutions made alkaline by ammonium hydroxide, in the presence of ammonium salts (but whose sulphides are soluble in dilute solutions of strong acids).

(20A) Preliminary Precipitation of the Group. — To 1 c.c. of the main bulk of the filtrate obtained in (**15**), which did not contain phosphates, add 1 drop of conc. HNO_3, and boil for a minute or more ①. Add ½ c.c. of NH_4Cl ② and warm again. (These two steps are not necessary in treating the filtrate from [**16**], from which phosphates were removed, since Fe was also removed and a large concentration of ammonium ③ salt added; it would be superfluous to add NH_4Cl. From this point, however, the filtrate from (**16**) should be treated in the same fashion as the one from (**15**).) To the sample from the HNO_3–NH_4Cl treatment above, or to 1 c.c. of the filtrate from (**16**), add NH_4OH to alkaline reaction and warm to coagulate any precipitate. If none forms, Fe, Al, and Cr are absent ①. Whether a precipitate has formed or not, pass H_2S into the mixture for a minute or more. If any further precipitate forms, or if a precipitate forms here for the first time, the whole filtrate from (**15**) or (**16**) must be treated for the presence of the Fe group by (**20**). Add the small sample mixture used above to the mixture obtained in (**20**) *after* the group has been precipitated. If no precipitate was formed in either of the trials above, Group 3 is absent. Treat the main portion of the solution from (**15**) or (**16**) by (**28A**) to test for Group 4, the alkaline earth group.

(20) Precipitation of the Group ③. If a precipitate was formed in the trial sample (**20 A**) heat the main portion of the solution from (**15**) or (**16**) to boiling (add 3 c.c. NH_4Cl to filtrate (**15**) ②) and pass in a stream of H_2S until the solution is saturated. Keeping the solution hot, add NH_4OH drop by drop until, after blowing any gas away from the surface of the liquid, you can still smell NH_3 distinctly, but not overpoweringly. (This step should be done very carefully because too great an excess of NH_4OH is distinctly undesirable ④.) Pass H_2S into the mixture until it ceases to smell of NH_3 ⑤. Allow the precipitate to settle, and add a drop or two of NH_4OH to see if precipitation is complete. Heat the mixture again and pass in H_2S for a minute. Heat the mixture and filter 1 c.c.; treat this with a drop of NH_4OH and H_2S to see if precipitation was complete. If more precipitate forms, pour this sample back into the main portion; add 1–2 drops of NH_4OH and pass in H_2S for a time longer. Continue this until no further evidence of precipitation is evident. Filter the mixture while hot, keeping the funnel covered ⑦ with a watch glass between pourings. Wash the precipitate with a mixture of hot H_2O to which a little $(NH_4)_2S$ ⑧ has been added. Treat the precipitate by (**21**) for separation of Co and Ni, and the filtrate ⑨ by (**28**) for the precipitation of Group 4. The precipitate may consist of $Fe(OH)_3$ ⑩, $Cr(OH)_3$, $Al(OH)_3$, FeS, Fe_2S_3 ⑩, CoS, NiS, MnS, and ZnS. (If the phosphates have been removed, the precipitate may, of course, consist of only the last four.)

(21) Separation and Detection of Cobalt and Nickel. — Transfer the precipitate obtained in (**20**) to a casserole, treat it with 5–10 c.c. (or more if the precipitate is large) of cold 5 per cent HCl (1 part 2*N* HCl to 2 parts H_2O) and stir the precipitate in the HCl thoroughly with a glass rod for three to four minutes. If a black precipitate of appreciable size ②

remains, filter and wash it first with cold 5 per cent HCl and then with hot H_2O. Treat the filtrate by (**22**) for the separation of Al and Zn. The precipitate ③, which may consist of CoS and NiS, is to be boiled with about 5–10 c.c. of aqua regia ($3HCl:1HNO_3$) until nothing more dissolves. Evaporate to 1–2 c.c., dilute to 5 c.c. with H_2O, and filter from the residue of free S ④. Make the filtrate just alkaline with NH_4OH, and divide into two equal portions. To the one add a few drops of dimethylglyoxime ⑤. A bright pinkish red precipitate indicates the presence of **Nickel** and is nickel dimethylglyoxime, $Ni([CH_3]_2N_2O_2H)_2$. To the other portion add 3 c.c. of NH_4Cl and 5 c.c. nitroso-beta-naphthol. A brick-red precipitate, insoluble in H_2SO_4, indicates the presence of **Cobalt** and is cobaltic nitroso-beta-naphthol ⑥ $Co(C_{10}H_6[NO]O)_3$. If it is not desired to estimate the amount of Co present, the above ammoniacal filtrate need not be divided, but simply treated with an excess of dimethylglyoxime, the red precipitate filtered, and the filtrate examined by looking down through it in a test-tube. A brown solution ⑦ indicates Co and is cobalt dimethylglyoxime, $Co([CH_3]_2N_2O_2H)_2$.

(**22**) **Separation of Aluminum and Zinc.** — Boil ⑧ the filtrate from (**21**), which may contain $AlCl_3$, $CrCl_3$, $FeCl_3$, $FeCl_2$, $MnCl_2$, and $ZnCl_2$, until the odor of H_2S is no longer detectable. To this solution add NaOH until the solution is just alkaline, and then add 3 c.c. more ⑨. The total volume should now be from 15 to 20 c.c. If it is not, dilute it to this volume with water ⑩. Boil the solution for two to three minutes to insure solution of any $Al(OH)_3$ and $Zn(OH)_2$ ⑩ which may have been precipitated and to insure precipitation of any $Cr(OH)_3$ ⑩ by hydrolysis. Filter and wash the precipitate with hot H_2O. This precipitate may consist of $Fe(OH)_3$, $Cr(OH)_3$, $Mn(OH)_2$, $MnO(OH)_2$ ⑪, and small amounts of $Ni(OH)_2$ and $Co(OH)_2$ ⑫. Treat it by

(23) for the separation and detection of Cr. Treat the filtrate by (26) for the separation and detection of Al.

(23) **Separation and Detection of Chromium.** — Transfer the precipitate obtained in (22) to a casserole, add 5–10 c.c. of H_2O and (gradually) ⑬ 1 g. of Na_2O_2 ⑭. Boil until the evolution of oxygen ceases. This is evidenced by the fact that the solution, after removing from the flame, no longer evolves small bubbles of gas after time enough has elapsed to permit boiling to cease. Filter and wash the precipitate with hot H_2O. Treat this precipitate, which may be $MnO(OH)_2$ and $Fe(OH)_3$, by (24) for the separation and detection of Mn. If the filtrate from this precipitate is a distinct yellow in color, the presence of **Chromium** is indicated. The yellow compound is Na_2CrO_4. Confirm it by the $Pb(C_2H_3O_2)_2$ test as outlined in (18).

(24) **Separation and Detection of Manganese.** — Dissolve the precipitate, which may consist of $Fe(OH)_3$ and $MnO(OH)_2$ ⑮ ⑯, from (23) in 5 c.c. of hot HCl by repeatedly pouring the latter over the filter. Evaporate this HCl filtrate to a few drops, add 7 c.c. of NH_4Cl ⑰, boil thoroughly to remove any dissolved air ⑱, and make distinctly alkaline with NH_4OH which has also been boiled ⑱. Filter immediately ⑱ and wash the precipitate, which may be $Fe(OH)_3$, with hot H_2O. Treat it by (25) for the detection of Fe. Pass H_2S into the filtrate, which may contain Mn as the chloride. A pink precipitate indicates the presence of **Manganese** and is MnS. If this precipitation is at all doubtful in color confirm the presence of Mn by a Na_2CO_3 bead test. To do this, make a bead as per instructions on p. 15. Scrape a small amount of the precipitate onto the bead by rubbing the latter through the precipitate on the filter. Heat the bead and MnS in the oxidizing portion of the flame until no specks can be observed in the molten bead while in the

flame. Remove the bead from the flame and, while it is still hot, pick up a small crystal of $KClO_3$ from a watch glass and hold the bead in the oxidizing portion of the flame. Remove while the evolution of oxygen from the $KClO_3$ in the bead is still going on, and allow to cool thoroughly. A bright green bead confirms Mn and is due to Na_2MnO_4 ⑲.

(25) **Detection of Iron.** — Dissolve the precipitate from (24) which may be $Fe(OH)_3$, in hot dilute HCl, and to the filtrate add 2 c.c. of $K_4Fe(CN)_6$ ⑳. A deep blue precipitate indicates the presence of **Iron** and is $Fe_4(Fe[CN]_6)_3$. Since this is a very sensitive test for Fe and the latter is very likely to be introduced accidentally in small quantities from rusty ironware, etc., a small precipitate may be viewed with suspicion.

(26) **Separation and Detection of Aluminum.** — To the filtrate from (22), which may contain $NaAlO_2$ and Na_2ZnO_2, add conc. HCl ㉑ drop by drop until the solution is just acid. Then add conc. NH_4OH carefully drop by drop until the solution is alkaline. Add 1 c.c. more ㉓, and boil. A white flocculent precipitate tending to retain air bubbles (if it has not been boiled too long) indicates the presence of **Aluminum** and is $Al(OH)_3$. It should always be confirmed. For confirmatory tests see (19). Treat the filtrate by (27).

(27) **Detection of Zinc.** — Pass H_2S into the ammoniacal filtrate from (26), which may contain Zn as $Zn(NH_3)_4(OH)_2$ ㉒, until the solution is saturated. A white precipitate indicates the presence of **Zinc** and is ZnS. If the precipitate is not definitely white ㉓ in color, filter and wash it with hot H_2O. Dissolve in 5–10 c.c. of hot HNO_3 by pouring the latter repeatedly through the filter. To the solution add 1–3 drops (not more) of a $0.3N$ $Co(NO_3)_2$ solution. Evaporate the mixture carefully to dryness, allowing the heat of the dish to evaporate the last few drops. Add

2 c.c. of 3*N* Na_2CO_3 solution. Evaporate to dryness again, and heat the residue very carefully until the blue of the cobalt disappears. Cool and moisten the residue with H_2O. A green residue, which is $CoZnO_2$, confirms the presence of Zn. (If the residue, because of overheating, becomes black, add a few drops of HNO_3 and repeat the rest of the test as given above ㉔.)

NOTES ON THE PRECIPITATION OF THE IRON GROUP

(Group 3)

1. The H_2S was previously removed (**15**), and the Fe^{++} oxidized with HNO_3 to see the effect of NH_4OH alone. Whereas this step is not essential, it oftentimes gives a helpful indication of the presence or absence of Al, Cr, and Fe, since the hydroxides of these trivalent elements are insoluble even in the presence of NH_4Cl. (See Note **9** below.)

* * *

2. NH_4Cl is added for the purpose of repressing the concentration of the OH^- ion by common ion effect (see *Theory*, pp. 110–11, etc.) and thus preventing the precipitation of $Mg(OH)_2$ at this point. This repression also minimizes the solvent effect of the NH_4OH on the amphoteric hydroxides such as $Al(OH)_3$. (See Note **13**, p. 90, and *Theory*, p. 122 *et seq.*) Only a small amount of NH_4Cl need be added at the beginning of this group since some is formed by neutralization of the HCl introduced in Group 2.

In the filtrate from the phosphate procedure no NH_4Cl is necessary since a high concentration of NH_4^+ ion was introduced in adding $NH_4C_2H_3O_2$.

* * *

3. The conditions under which this group is precipitated greatly affect the ease with which the group precipitate can be filtered. The condition of the precipitate, particularly of the sulphides contained therein, has a great

deal to do with this and in turn depends largely on amount of excess NH_4OH present. (See Note 4 following.) The best conditions for precipitating this group were investigated by Vestner (*Dissertation*, München, 1909, p. 37), and are given here. They should be closely adhered to, otherwise considerable time may be lost in filtering.

* * *

4. Excess of NH_4OH is to be very carefully avoided because, in the presence of such an excess and in the presence of excess $(NH_4)_2S$ which would be formed from it, NiS is distinctly soluble and causes filtration to be slowed up considerably. It imparts a dark brown color to the filtrate and cannot be removed by refiltration. The NiS may be precipitated from the filtrate by boiling until the odor of NH_3 is almost gone. The nature of this brown solution is not known but may be a colloidal solution of NiS. It seems to form particularly in the presence of ammonium polysulphide $(NH_4)_2S_2$. The latter is formed from the oxidation of $(NH_4)_2S$ by the air, liberating free S, which combines with another molecule of $(NH_4)_2S$:

$$2(NH_4)_2S + O_2 \rightarrow 4NH_3 + 2H_2O + 2S.$$
$$(NH_4)_2S + S \rightarrow (NH_4)_2S_2.$$

Other sulphides of the group may be affected in this way to a lesser extent. For this reason H_2S (which forms $(NH_4)_2S$ with the small excess of NH_4OH [see Note **5** below]) is used as a precipitating agent instead of prepared $(NH_4)_2S$, which on standing about forms appreciable quantities of $(NH_4)_2S_2$.

In addition to the effect upon the sulphides, too large an excess of NH_4OH would have a slight solvent effect upon the amphoteric hydroxides, particularly $Al(OH)_3$:

$$Al(OH)_3 + NH_4OH \rightarrow NH_4AlO_2 + 2H_2O.$$
$$Cr(OH)_3 + NH_4OH \rightarrow NH_4CrO_2 + 2H_2O.$$

The latter reaction is reversed by boiling. This is desirable because Mg (and Zn) might be precipitated as $MgCrO_2$ and $ZnCrO_2$ if the amount of chromite in the solution were appreciable.

* * *

5. Though too large an excess of NH_4OH is undesirable, yet there must be a sufficient amount present to form enough $(NH)_2S$ according to the reaction:

$$2NH_4OH + H_2S \rightarrow (NH_4)_2S + 2H_2O$$

to precipitate all the sulphides of the elements in the group. For this reason mere alkalinity to litmus paper is not sufficient, and it is therefore recommended that the solution smell moderately of NH_3 (i.e., so that one need not draw one's head away). The sulphides of the group may be incompletely precipitated unless this is so. Thus the precipitate is allowed to settle and a small amount of NH_4OH added to test for complete precipitation.

A concentration of sulphide ion great enough to precipitate the more soluble sulphides of Group 3 is reached by virtue of the fact that $(NH_4)_2S$ is formed according to the above equation. The highly ionized salt $(NH_4)_2S$ has a sulphide ion concentration about one billion times as great as that of the weakly ionized H_2S. (See *Theory*, pp. 160–61.)

* * *

6. The mixture is filtered hot because heating tends to coagulate the amorphous sulphides and hydroxides; also because the filtrate will be less viscous, of course. The funnel is kept covered to prevent too much oxidation of the sulphides to soluble sulphates and to prevent volatilization of the decomposition products of $(NH_4)_2S$. (See next note.)

* * *

7. The precipitate is washed with $(NH_4)_2S$ in order that an excess of it may be always present and covering the precipitate. That which was present from the original

filtrate tends to volatilize, giving NH_3 and H_2S, and to be oxidized by air (as indicated by equation in Note **4**, this section).

Removal of $(NH_4)_2S$ in this manner would expose the sulphides of the group to oxidation by air to soluble sulphates, causing irregularities in the procedure thereby.

* * *

8. The filtrate from Group 3 may be a light yellow because of the formation of small amounts of $(NH_4)_2S_2$. This is to be removed as per later instructions before the precipitation of Group 4. If the filtrate is dark in color, however, it means that Ni has gone through as per Note **4** (this section). It should be removed by boiling as outlined in that note, filtered, and added to the original precipitate for the group.

* * *

9. The nature of the various precipitates occurring in this group is accounted for as follows: Al, Cr, and Fe (ferric) are sufficiently insoluble to be precipitated as hydroxides even in the presence of NH_4Cl (see *Theory*, pp. 110–11). Though the hydroxides of all the divalent metals are insoluble, the OH^- concentration is not sufficiently great to exceed their solubility products and they are not precipitated. This is true for ferrous Fe, Co, and Mn. In the case of the remaining two, while their hydroxides are insoluble, they have the property of forming the ammonia complexes represented by $M(NH_3)_4^{++}$ and are therefore not precipitated. (See *Theory*, p. 136.) Ferrous and manganous salts are easily oxidized, however, and begin to precipitate after a time as $Fe(OH)_3$ and $MnO(OH)_2$ (which is more insoluble than $Mn(OH)_2$); Co is also oxidized, but $Co(OH)_3$ is not sufficiently insoluble to precipitate. On passing in H_2S, the sulphides of the metals not already precipitated come down because they are more insoluble than the corresponding hydroxides. Thus even the small concentration of Zn ion from the very weakly dissociated complex $Zn(NH_3)_4^{++}$

is sufficiently great to exceed the solubility product of ZnS, because the concentration of the $S^=$ ion is relatively high. $Fe(OH)_3$ is converted to Fe_2S_3 by $(NH_4)_2S$ but this does not happen in the case of Al and Cr. Their sulphides are not stable in the presence of water and would be immediately hydrolyzed if formed (see *Theory*, p. 132). Any ferrous Fe is precipitated as black FeS.

The colors of the precipitates are as follows: $Al(OH)_3$, white; $Fe(OH)_3$, brownish red; $Cr(OH)_3$, grayish green; Fe_2S_3, black; FeS, black; CoS, black; NiS, black; MnS, pink; ZnS, white.

NOTES ON THE SEPARATION AND DETECTION OF GROUP 3 METALS

1. The separation of Co and Ni from the rest of the elements of this group depends upon the fact that the hydroxides and sulphides of the latter are readily soluble in cold dilute HCl while the sulphides of Co and Ni are only very slowly soluble under these conditions. This seems a rather anomalous condition when it is remembered that CoS and NiS cannot be precipitated from an acid solution of this strength by H_2S, except over a long period of time. The explanation lies in the fact that the sulphides of Co and Ni are capable of existing in at least two, and possibly three, different modifications, called the alpha, beta, and gamma forms. When the sulphides are precipitated they come down in the alpha form, which is soluble in dilute HCl, but on standing, and particularly on warming, go rather rapidly over to the gamma form, which is only very slowly soluble in cold dilute HCl.

In spite of these facts, however, the separation with cold dilute HCl is not perfect; small amounts of $CoCl_2$ and $NiCl_2$ are nearly always found in the filtrate but cause no particularly disturbing consequences during the analysis of the filtrate. (See Note **12** below.)

The hydroxides and sulphides of the other elements

are soluble in cold dilute HCl because of the reduction respectively of the OH^- and $S^=$ ion concentrations as a result of the formations of the weakly ionized compounds, H_2O and H_2S. (See *Theory*, p. 117 *et seq.*)

* * *

2. A very small black or grayish black precipitate is often formed when Co and Ni are absent. This may be due to small amounts of FeS or other dark-colored precipitates adhering to, or enclosed in, the free sulphur which results from the air oxidation of H_2S.

* * *

3. If it is not desired to estimate quantities, Co (and Ni, if Co is absent), may be tested for directly at this point by means of a borax bead test. Co gives a blue bead which will cover up the reddish brown bead of Ni, even though the NiS constitute 96 per cent of the total precipitate. If Co is absent, of course, the reddish brown bead of Ni is evidence of its presence. The bead tests are made in the usual way by heating a looped wire, plunging it into some solid borax, $Na_2B_4O_7$, and melting this in the flame to a clear glasslike bead. The bead, after some cooling, is then scraped through the precipitate on the filter until some of the precipitate adheres to it. Until experience is gained in finding approximately the amount necessary to give a satisfactory bead, only a small amount of precipitate should be taken on the bead at a time. Too much will make the bead opaque so that its color cannot be easily determined. As soon as the precipitate is on the bead, the whole should be heated in the oxidizing portion of the flame until, examined in the flame, the bead contains no evidence of any specks floating about and the whole looks like a uniform mass of molten liquid. The common tendency is to heat the bead altogether too short a time. In order to be safe the bead should be heated for at least five minutes and, when removed from the flame and allowed to cool, should be clear, transparent,

and perfectly uniform. A deep blue color indicates the presence of cobalt and is $Co(BO_2)_2.2NaBO_2$. In the presence of Co, nothing can be told about Ni by the bead test. The mixed sulphides are dissolved in aqua regia and Ni determined by means of dimethylglyoxime. The bead reactions for both sulphides are as follows:

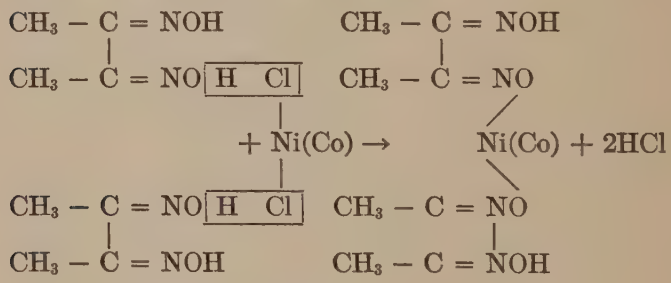
$$2(Co,Ni)S + 2Na_2B_4O_7 + 3O_2(air) \rightarrow [Co,Ni](BO_2)_2.2NaBO_2 + 2SO_2.$$

* * *

4. Co and Ni sulphides dissolve readily in aqua regia to form the corresponding chlorides. The reaction is the same as that for HgS (see Note **7**, p. 61).

* * *

5. Dimethylglyoxime is an organic compound having a hydrogen atom which is easily replaced by a metal. With Ni salts it gives a bright pinkish red precipitate and with Co a brown solution. Both of these reactions are very sensitive, particularly the former, which is capable of detecting as little as 0.0000003 g. of Ni. The reactions may be formulated as follows:



* * *

6. α-Nitroso-β-Naphthol, another organic compound, gives a red precipitate with Co salts which is not dissolved by H_2SO_4. This distinguishes it from Ni, Fe(-ic), and other salts which give a similar color but whose precipitates

are soluble in the acid. α-Nitroso-β-Naphthol gives more satisfactory results when made up in very dilute alkaline solution rather than in strong acetic acid solution. In the latter case there is danger that the α-Nitroso-β-Naphthol itself may be precipitated on dilution. The Co salts are first oxidized to the cobaltic condition by the reagent and the following reaction takes place:

$$3C_{10}H_6(NO)OH + CoCl_3 \rightarrow (C_{10}H_6[NO]O)_3Co + 3HCl.$$

* * *

7. The brown solution of cobalt dimethylglyoxime (see Note **5** above) is a sensitive test for Co and is used for the colorimetric estimation of it.

* * *

8. It is very important to boil the solution at this point to remove the H_2S formed from the solution of the sulphides in HCl. If the H_2S is not removed, ZnS, which is insoluble in alkaline solution, may be precipitated out of place when the solution is made alkaline with NaOH in the next step.

* * *

9. An excess of NaOH is necessary in order to insure the complete solution of the amphoteric hydroxides of Zn and Al. (See *Theory*, p. 126.)

* * *

10. Water is added and the solution boiled at this point to insure the precipitation of $Cr(OH)_3$, which, being amphoteric, dissolves at first in the same manner as do Al and Zn hydroxides (see Note **9** above). $Cr(OH)_3$ is reprecipitated by hydrolysis, on boiling, as shown by the following equilibrium:

$$Cr(OH)_3 + OH^- \rightleftarrows CrO_2^- + 2H_2O.$$

$Zn(OH)_2$ may be reprecipitated in the same way, but not when there is an excess of OH^- present. $Al(OH)_3$ is not reprecipitated under these circumstances.

11. Mn may be present in two forms here, because of the oxidation of $Mn(OH)_2$ to $MnO(OH)_2$ by the air. This is evidenced by a change in color of the precipitate, since $Mn(OH)_2$ is white and $MnO(OH)_2$ is dark brown. After Na_2O_2 has been added the conversion is complete and only $MnO(OH)_2$ is present. This precipitate has a peculiar characteristic of sticking rather tenaciously to the sides of an evaporating dish.

* * *

12. As stated in Note **1** above, CoS and NiS are not entirely insoluble in cold dilute HCl. Thus small amounts of both are always dissolved. This results in a small greenish precipitate of $Co(OH)_2$ and $Ni(OH)_2$ on subsequent addition of NaOH and is misleading so far as Fe, Mn, and Cr are concerned. In general, however, the precipitate is so small that its presence may be neglected.

* * *

13. The reason for the gradual addition of Na_2O_2 is explained in Note **9**, p. 88 (phosphate separation).

* * *

14. See previous notes on the detection of Cr (phosphate separation), Notes **10C** and **11**, p. 89.

* * *

15. $MnO(OH)_2$ dissolves in HCl with the formation of $MnCl_2$ and Cl_2, which is expelled by boiling:

$$MnO(OH)_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 3H_2O.$$

* * *

16. The procedure may be somewhat shortened at this point if an estimation of the quantity of Fe present is not desired: the precipitate of $Fe(OH)_3$ and $MnO(OH)_2$ is tested with a Na_2CO_3 bead in the oxidizing flame (for directions see (**24**)). The reaction is as follows:

$$2MnO(OH)_2 + 2Na_2CO_3 + O_2 \rightarrow Na_2MnO_4 + 2H_2O + 2CO_2.$$

$Fe(OH)_3$ imparts only a faint yellow to the bead and does not interfere.

The $Fe(OH)_3$ and $MnO(OH)_2$ remaining may now be dissolved in HCl, and KCNS added. The presence of Fe is indicated by a deep red coloration due to $Fe(CNS)_3$:

$$FeCl_3 + 3KCNS \rightarrow Fe(CNS)_3 + 3KCl.$$

This is a very sensitive test for Fe, and unless the red is fairly dark, only traces of Fe (which might be due to rust from apparatus, etc.) should be reported. The Mn does not interfere.

* * *

17. NH_4Cl is added at this point to prevent the precipitation of $Mn(OH)_2$. This is an application of the common ion effect (see *Theory*, p. 110).

* * *

18. These solutions are boiled to remove any dissolved air which might tend to oxidize the Mn and cause the precipitation of $MnO(OH)_2$.

* * *

19. The reaction for the Mn bead test is given in Note **16** above.

* * *

20. See Note **4**, p. 86 (phosphate separation), for the Fe reaction.

* * *

21. See Note **13**, p. 90 (phosphate separation), for reasons for adding HCl before adding NH_4OH.

* * *

22. The separation of Al from Zn depends upon the fact that the latter forms a complex ion $Zn(NH_3)_4^{++}$ and that the hydroxide corresponding to this ion is not insoluble. Al forms no such ion with NH_3 and is therefore precipitated as $Al(OH)_3$ (see *Theory*, p. 136).

23. The white precipitate of ZnS is sometimes obscured by the formation of small amounts of a black precipitate. The latter is probably due to traces of Co, Ni, or Fe which have been carried through (perhaps in colloidal form).

* * *

24. The confirmatory test for Zn depends upon the formation of green $CoZnO_2$ and is a fairly sensitive test when carried out properly. Care must be exercised not to use too much $Co(NO_3)_2$ because the latter forms black CoO on ignition. This would obscure the green.

SUMMARY OF GROUP 3

The principles of separation applied in this group are:

1. (Of Group 3 from the remaining groups) that the sulphides and hydroxides of this group are insoluble in solutions made alkaline with NH_4OH in the presence of NH_4 salts.

2. (Of Co and Ni from Fe, Mn, Cr, Al, and Zn) that CoS and NiS are only slowly soluble in cold dilute HCl.

3. (Of Co from Ni) that the nitroso-beta-naphthol salt of the former and the dimethyl-glyoxime salt of the latter are insoluble in dilute alkaline solutions.

4. (Of Fe, Mn, and Cr from Al and Zn) that $Fe(OH)_3$, $Cr(OH)_3$, and $Mn(OH)_2$ or $MnO(OH)_2$ are precipitated in the presence of NaOH in excess, when the solution is diluted and boiled.

5. (Of Fe and Mn from Cr) that $Fe(OH)_3$ and $Mn(OH)_2$ or $MnO(OH)_2$ are not converted to soluble compounds on boiling with Na_2O_2 and H_2O.

6. (Of Fe from Mn) that Mn is not precipitated by NH_4OH in the presence of NH_4 salts, when it is in the divalent form.

7. (Of Al from Zn) that $Zn(OH)_2$ is not precipitated by NH_4OH.

Equations on Group 3 Metals

COBALT

1. Cobalt nitrate and ammonium hydroxide (in presence of ammonium salts).
2. Cobalt nitrate and ammonium sulphide.
3. Cobalt sulphide and cold dilute hydrochloric acid.
4. Cobalt sulphide and aqua regia.
5. Cobalt chloride and nitroso-beta-naphthol (no reaction need be written, since the product is rather complex).
6. Cobalt chloride and dimethylglyoxime. (See previous equation.)
7. Cobalt sulphide, borax, and oxygen (atmospheric).

NICKEL

1. Nickel nitrate and ammonium hydroxide.
2. Nickel ammonia nitrate and ammonium sulphide.
3. Nickel sulphide and cold dilute hydrochloric acid.
4. Nickel sulphide and aqua regia.
5. Nickel chloride and dimethylglyoxime. (See eq. 6 under Cobalt.)
6. Nickel chloride and nitroso-beta-naphthol. (See eq. 5 under Cobalt.)
7. Nickel sulphide, borax, and oxygen (atmospheric).

CHROMIUM

1. Chromium nitrate and ammonium hydroxide.
2. Chromium hydroxide and ammonium sulphide.
3. Chromium hydroxide and dilute cold hydrochloric acid.
4. Chromium chloride and sodium hydroxide (in excess).
5. Sodium chromite and water (boiling).
6. Chromium hydroxide, sodium peroxide, and water.
7. Sodium chromate and lead acetate.

ALUMINUM

1. Aluminum nitrate and ammonium hydroxide.
2. Aluminum hydroxide and ammonium sulphide.
3. Aluminum hydroxide and dilute cold hydrochloric acid.
4. Aluminum chloride and sodium hydroxide in excess.
5. Sodium aluminate and water (boiling).
6. Sodium aluminate and hydrochloric acid.
7. Aluminum chloride and ammonium hydroxide.
8. Aluminum hydroxide and hydrochloric acid.
9. Aluminum chloride and aluminon reagent. (See equations for Aluminum on p. 92.)

ZINC

1. Zinc nitrate and ammonium hydroxide.
2. Zinc ammonia nitrate and ammonium sulphide.
3. Zinc sulphide and cold dilute hydrochloric acid.
4. Zinc chloride and sodium hydroxide in excess.
5. Sodium zincate and water (boiling).
6. Sodium zincate and hydrochloric acid.
7. Zinc chloride and ammonium hydroxide.
8. Zinc ammonia chloride and hydrogen sulphide.
9. The reactions in the confirmatory test for Zinc are not clearly understood, even though it is fairly well established that the product is $CoZnO_2$. This may be a compound or merely a solid solution of oxides.

IRON

1. Ferric chloride and hydrogen sulphide (Group 2).
2. Ferrous chloride and nitric acid.
3. Ferric nitrate and ammonium hydroxide.
4. Ferric hydroxide and ammonium sulphide.
5. Ferric sulphide and cold dilute hydrochloric acid.
6. Ferric chloride and sodium hydroxide in excess.
7. Ferric hydroxide, sodium peroxide, and water.
8. Ferric hydroxide and hydrochloric acid.

9. Ferric chloride and ammonium hydroxide.
10. Ferric hydroxide and hydrochloric acid.
11. Ferric chloride and potassium ferrocyanide.

MANGANESE

1. Manganous nitrate and ammonium hydroxide (in the presence of ammonium salts).
2. Manganous nitrate and ammonium sulphide.
3. Manganous sulphide and cold dilute hydrochloric acid.
4. Manganous chloride and sodium hydroxide in excess.
5. Manganous hydroxide and atmospheric oxygen.
6. Manganous hydroxide, sodium peroxide, and water.
7. Hydrated manganous dioxide and hydrochloric acid.
8. Manganous chloride and ammonium hydroxide (in presence of ammonium salts).
9. Manganous chloride and ammonium sulphide.
10. Manganous sulphide, sodium carbonate, and oxygen (from $KClO_3$).

Questions on Group 3 Metals

(See also *Theory*, pp. 168–174.)

1. In boiling the filtrate from Group 2, a white finely divided precipitate often forms. What is this precipitate, and what causes it to be formed?
2. Why is the filtrate from Group 2 boiled with a few drops of concentrated HNO_3 before starting the analysis of Group 3?
3. State what differences in the precipitate formed by the addition of NH_4OH at the beginning of Group 3 might be caused by failure to add NH_4Cl.
4. Why does NH_4OH fail to precipitate the hydroxides of Zn and Ni at the beginning of Group 3? Why does it fail to precipitate the hydroxides of Co and Mn?
5. Do any of the hydroxides precipitated by NH_4OH at the beginning of Group 3 undergo change when H_2S is passed into the solution? Why do not all of them undergo change? Explain in detail.

6. If NH_4OH fails to give a precipitate at the beginning of Group 3, what conclusions are warranted?
7. Why is not the precipitate of Fe(-ic), Cr, and Al hydroxides filtered and analyzed separately from the sulphides of Co, Ni, Mn, and Zn? If this could be done successfully, the analysis of Group 3 would be greatly simplified.
8. Give the colors and formulas of all the compounds which appear as precipitates in Group 3.
9. Why is the precipitate with NH_4OH and H_2S, at the beginning of Group 3, not always black?
10. In filtering the precipitate at the beginning of Group 3, why is it advisable to keep the funnel covered?
11. Give two reasons why too large an excess of NH_4OH should not be added at the beginning of Group 3.
12. Why is the concentration of the sulphide ion much greater in Group 3 when the solution is saturated with H_2S than at the beginning of Group 2 when the solution is saturated with H_2S?
13. Why is it always advisable to filter a precipitate while hot, if possible?
14. To what error does a dark brown filtrate from Group 3 point?
15. What is the basis of the separation of Co and Ni from the rest of the elements in Group 3? Will CoS and NiS eventually dissolve in HCl (dilute)?
16. Explain the fact that CoS and NiS will not dissolve readily in HCl and yet cannot be precipitated from a much more weakly acid solution.
17. Explain why Ni dimethylglyoxime is not precipitated from an acid solution. (Dimethylglyoxime is a weak acid.)
18. In making the borax bead test for Co or Ni, why is it necessary to hold the bead in the oxidizing portion of the Bunsen flame?
19. Why is it important to boil the HCl filtrate from the separation of Co and Ni from the rest of Group 3?
20. When the filtrate from the separation of CoS and NiS is made alkaline with NaOH, a small flocculent precipitate often forms, even when Al, Cr, Fe, Mn, and Zn are absent. Explain.
21. What is the basis of the separation of Fe and Mn from Al and Zn?

22. Cr is amphoteric as well as Al and Zn? Why does it not remain dissolved in the excess NaOH?
23. Assuming that no complex ions are formed, would it be possible for a hydroxide to be soluble in NH_4OH and not in NaOH? Explain your answer.
24. Explain the basis of the separation of Cr from Fe and Mn.
25. When the precipitate of the hydroxides of Fe, Mn, and Cr is treated with Na_2O_2 and H_2O, it turns very dark. Explain.
26. Given a piece of pure lead metal and a piece of pure chromium metal, how would you prepare $PbCrO_4$?
27. What is the basis of the separation of Fe from Mn?
28. Why are the solutions of NH_4Cl and NH_4OH, added in the Mn test, boiled thoroughly before addition?
29. Name and give equations for two confirmatory tests for Mn.
30. Why is $KClO_3$ used in the bead test for Mn? Would it be possible to get the Mn bead without use of $KClO_3$?
31. Why is $Fe(OH)_3$ not dissolved in HNO_3, in making the confirmatory test for Fe with KCNS?
32. What is the basis of the separation of Al from Zn?
33. What precautions must be taken in the confirmatory test for Zn?

TABLE 7

GROUP 4 METALS

(*Ba, Sr, Ca, Mg*)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Sol. 1 (Table 6)	$(NH_4)_2CO_3$, NH_4OH, C_2H_5OH	White ppt.	Group 4 pres.	$BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3.(NH_4)_2CO_3$	Group 5
2.	Ppt. 1	$HC_2H_3O_2$	Solution	X	X	$Ba(C_2H_3O_2)_2$, $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$, $Mg(C_2H_3O_2)_2$
3.	Sol. 2	$NH_4C_2H_3O_2$, K_2CrO_4	Yellow ppt.	Ba pres.	$BaCrO_4$	$CaCrO_4$, $SrCrO_4$, $MgCrO_4$, etc.
4.	Ppt. 3	HCl, Flame	Green flame	Ba conf.	X	$BaCl_2$
5.	Sol. 3	NH_4OH, C_2H_5OH	Yellow ppt.	Sr pres.	$SrCrO_4$	$CaCrO_4$, $MgCrO_4$

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
6.	Ppt. 5	H_2O, $(NH_4)_2SO_4$, HCl, flame	Red flame	Sr. conf.	X	$SrCl_2$
7.	Sol. 5	$(NH_4)_2C_2O_4$	White ppt.	Ca pres.	CaC_2O_4	MgC_2O_4
8.	Ppt. 7	H_2SO_4, C_2H_5OH	White ppt.	Ca conf.	$CaSO_4$	X
9.	Sol. 7	NH_4OH, Na_2HPO_4	White ppt.	Mg. pres.	$MgNH_4PO_4$	X
10.	Ppt. 9	H_2SO_4, C_2H_5OH	Partial solution	Ba, Sr, Ca phosphates removed	($BaSO_4$, $CaSO_4$), ($SrSO_4$)	$MgSO_4$
11.	Sol. 10	NH_4OH, Na_2HPO_4	White ppt.	Mg conf.	$MgNH_4PO_4$	X

PRECIPITATION AND ANALYSIS OF THE ALKALINE EARTH GROUP (GROUP 4)

(Ba, Sr, Ca, Mg)

Definition. — Those metals whose carbonates are insoluble in alkaline alcoholic solutions in the presence of ammonium salts (but whose sulphides and hydroxides are soluble in alkaline and acid solutions and water).

(28A) **Preliminary Precipitation of the Group.** — Boil 1 c.c. of the filtrate from (20) (or the filtrate from the last group present, if Group 3 is absent) gently, to remove H_2S. To this solution add 1 c.c. of $(NH_4)_2CO_3$ reagent and 1 c.c. of alcohol. Shake the mixture and let it stand for fifteen minutes or more. A white flocculent precipitate indicates the presence of **Group 4.** Acidify the mixture with dilute HCl, add it to the main bulk of the filtrate from above, and treat the whole by (28). If no precipitate is formed on standing for half an hour, the group is absent. Pass directly to (33).

(28) **Precipitation of the Group.** — Evaporate the filtrate from (20) (or the last group analyzed) to a volume of about 6–8 c.c. Filter from any precipitate ① (boil with torn-up pieces of filter paper and filter repeatedly if the precipitate does not filter well at first). If any salts ② have crystallized out during the process of evaporation, these may also be discarded. To the filtrate, add 8 c.c. of $6N$ $(NH_4)_2CO_3$ (in NH_4OH) ③ and 10 c.c. of 95 per cent C_2H_5OH (grain alcohol). Shake the precipitate vigorously for ten minutes or more, or let it stand for at least a half-hour with occasional shaking, before filtering. (This is a particularly important

point! ④.) Filter, using suction, and wash the precipitate with 5 c.c. of $(NH_4)_2CO_3$ reagent. Treat the precipitate, which may consist of $BaCO_3$, $CaCO_3$, $SrCO_3$, and $MgCO_3.(NH_4)_2CO_3$ ④ by (**29**) for Ba, and the filtrate by (**32**) for the detection of Na and K.

(**29**) **Detection of Barium.** — Pour a hot 5 c.c. portion of $HC_2H_3O_2$ (more if necessary) over the filter repeatedly, to dissolve ⑤ the carbonates. Rinse out the vessel from which the $HC_2H_3O_2$ solution was last poured with a little H_2O, pouring this over the filter to wash down any adhering solution. Evaporate ⑥ the filtrate to 1 c.c. or a little less and add 5 c.c. of $NH_4C_2H_3O_2$ ⑦ and 5 c.c. H_2O. Heat the solution to boiling and add 1 c.c. of K_2CrO_4 drop by drop ⑧, warming and shaking after each addition ⑨. If a large precipitate ⑩ forms, add 2 c.c. more of K_2CrO_4, boil and shake as before. Finally, keep the solution almost at the boiling point for several minutes, and filter. If the filtrate is turbid, warm a few minutes longer; continue this until the filtrate is clear. A yellow precipitate indicates the presence of **Barium** and is $BaCrO_4$ ⑪. Wash this precipitate *thoroughly* with hot H_2O and dissolve in hot HCl. Apply the flame test for Ba to this filtrate by means of a platinum wire. A yellowish green flame indicates Ba. This confirmatory test for Ba is not necessary unless large quantities of Sr are found in the next procedure ⑬.

(**30**) **Detection of Strontium.** — To the filtrate from (**29**) add NH_4OH ⑭ to alkaline reaction. Warm the solution until it just cannot be comfortably held in the hand and then add 10 c.c. of C_2H_5OH, a few c.c. at a time, making sure that the solutions are thoroughly mixed after each shaking ⑮. (Any local and temporary precipitation at the top of the solution upon addition of C_2H_5OH and before shaking, should be disregarded ⑮.) Cool the solution thoroughly under the tap and allow it to stand for several minutes. A yellow

precipitate indicates the presence of **Strontium** and is $SrCrO_4$ ⑯. It should always be confirmed ⑰. Filter the precipitate, using suction if necessary. If the precipitate, which must be filtered cold, tends to run through the paper, shake it repeatedly with torn-up pieces of filter paper and filter until clear. Treat the filtrate by (**31**) for the detection of Ca and confirm the presence of Sr by repeatedly pouring 5 c.c. hot H_2O ⑱ over the filter containing the $SrCrO_4$. To the filtrate add 2 c.c. of $(NH_4)_2SO_4$, warm, and allow it to stand for a few minutes ⑲. Filter any precipitate, wash thoroughly, and dissolve it by pouring hot HCl ⑲ over the filter. Apply the flame test for Sr to this filtrate. A rich bright red flame indicates the presence of Sr.

(**31**) **Detection of Calcium.** — Dilute the filtrate from (**30**) to 40 c.c. with H_2O and add 3 c.c. of $(NH_4)_2C_2O_4$ ⑳. Let the solution stand for fifteen minutes unless a precipitate forms sooner. A white precipitate (which may look yellow in a yellow solution) indicates the presence of **Calcium** and is CaC_2O_4 ㉑. If there is a precipitate, heat the mixture almost to boiling, add 4 c.c. more of $(NH_4)_2C_2O_4$, and warm for a few minutes ㉒. Filter, wash the precipitate thoroughly, and confirm it. Treat the filtrate by (**32**) for Mg. To confirm ㉓ the presence of Ca, dissolve the CaC_2O_4 in a mixture of 3 c.c. of $2N$ H_2SO_4 and 2 c.c. of C_2H_5OH by pouring the mixture through the filter repeatedly. To the filtrate add 5 c.c. of C_2H_5OH and allow to stand for five minutes. A white precipitate, which is $CaSO_4$, confirms the presence of Ca.

(**32**) **Detection of Magnesium.** — To the filtrate from (**31**) add 3 c.c. of conc. NH_4OH ㉔ and 10 c.c. of Na_2HPO_4. Shake the mixture and allow it to stand for half an hour unless an appreciable precipitate forms sooner. A white crystalline precipitate ㉕ indicates the presence of **Magnesium** and is $MgNH_4PO_4$.

NOTES ON THE SEPARATION AND DETECTION OF THE ALKALINE EARTHS

1. The solution is evaporated to reduce its bulk to workable size and to remove any $(NH_4)_2S$ and free S formed by oxidization. The reactions involved are as follows:

$$(NH_4)_2S \rightarrow \nearrow NH_3 + H_2S \nearrow.$$
$$2H_2S + O_2 \rightarrow 2H_2O + 2S.$$

The NH_3 and H_2S which is not oxidized are volatilized from the solution and the S is filtered out. The torn filter paper is used to help coagulate any colloidal S which might otherwise run through the filter paper. (See section on Treatment of Precipitates under "General Technique," p. 13.)

* * *

2. Because fairly large amounts of ammonium salts have been added, particularly in the phosphate procedure, some may be crystallized out at this point. They have no effect upon the subsequent procedure and may be discarded.

* * *

3. $BaCO_3$, $SrCO_3$, and $CaCO_3$ are not completely insoluble in the presence of a moderate excess of the $CO_3^=$ ion. $MgCO_3$ is quite soluble under these conditions. The solubility of the former three is probably due to the hydrolysis of $(NH_4)_2CO_3$ to form the HCO_3^- ion, the bicarbonates of Ba, Sr, and Ca being distinctly soluble:

$$(NH_4)_2CO_3 + HOH \rightleftarrows NH_4OH + NH_4^+ + HCO_3^-.$$

Since the $(NH_4)_2CO_3$ is made up in $6N$ NH_4OH there is a fairly large excess of the latter present. This tends to reverse the hydrolysis and thus diminish the amount of HCO_3^- ion present. This condition, together with a large excess of the $CO_3^=$ ion supplied by the rather large amount of $(NH_4)_2CO_3$ used, and in the presence of a

fairly high concentration of alcohol, brings about practically complete precipitation of the carbonates of Ba, Sr, and Ca. If the solution is kept cold, Mg is also completely precipitated as a double carbonate, $MgCO_3.(NH_4)_2CO_3.4H_2O$ when the $CO_3^=$ concentration is sufficiently high.

The effect of the alcohol may be explained as follows: salts in general are not so soluble in pure alcohol as they are in pure water. Hence they will be more insoluble in water-alcohol mixtures than they are in water alone. Thus $SrCrO_4$ dissolves to the extent of 1.22 g. in 100 c.c. of pure water at room temperature but only to the extent of 0.002 g. in 100 c.c. of a solution of alcohol and water which is 53 per cent alcohol by volume, at the same temperature. In this way any slight solubility which the carbonates of the alkaline earth elements might have in water is reduced to negligible amounts by the presence of alcohol.

* * *

4. Contrary to the usual course of ionic reactions, the precipitation of the alkaline earth carbonates takes place rather slowly. This is particularly true of Mg and Ca. Therefore it is important to let the mixture stand for a considerable time. Failure to do this may introduce serious errors into the analysis of the group.

* * *

5. The carbonates of the alkaline earths dissolve in $HC_2H_3O_2$ by virtue of the formation of the weakly ionized and unstable H_2CO_3 (see *Theory*, p. 157).

* * *

6. An excess of $HC_2H_3O_2$ is used to insure complete solution of all the carbonates. This excess is then evaporated away so as to reduce the acid concentration, which would have a solvent effect upon the $BaCrO_4$ to be precipitated. (See Note **11** below.)

7. The $NH_4C_2H_3O_2$ is added to reduce the acidity of the $HC_2H_3O_2$ by the common ion effect and thus render the $BaCrO_4$ more insoluble. (See previous note. See also *Theory*, p. 102.)

* * *

8. The precipitating reagent, K_2CrO_4, is added drop by drop to completely precipitate the Ba before any great excess of the reagent is present; for, in the presence of large amounts of Ba, appreciable amounts of Sr might be precipitated by the sudden addition of a large excess of the reagent.

* * *

9. The precipitate is warmed and shaken after each addition of the reagent to facilitate the formation of larger particles of the precipitate (see "General Notes on Laboratory Technique," p. 13). $BaCrO_4$, particularly, has the tendency to come down in rather finely divided form and run through the filter paper.

* * *

10. Even though the first addition of K_2CrO_4 is sufficient to precipitate all the Ba which may ordinarily be present, an excess is added for complete precipitation by the common ion effect, in case any large quantity of Ba is present.

* * *

11. The separation of Ba from Sr, Ca, and Mg is due to the fact that $BaCrO_4$ is much more insoluble than the chromates of the others (see table, p. 218). It is the only one which can be precipitated in weakly acid solution when present in ordinary amounts. All chromates become increasingly soluble as the concentration of the H^+ ion is increased. This is due to the formation of the $HCrO_4^-$ and $Cr_2O_7^=$ ions, according to the equilibria:

$$H^+ + CrO_4^= \rightleftarrows HCrO_4^-, \quad 2HCrO_4^- \rightleftarrows Cr_2O_7^= + H_2O.$$

(See *Theory*, p. 161.)

12. $BaCrO_4$ is soluble in HCl for reasons brought out in the previous note. It should be washed thoroughly to remove adhering K_2CrO_4, since the potassium flame might partially obscure that of Ba.

* * *

13. $SrCrO_4$ is so soluble under the conditions which permit the precipitation of $BaCrO_4$ that, unless inordinately large amounts of Sr are present, any precipitate obtained can be only $BaCrO_4$.

* * *

14. NH_4OH is added to destroy the H^+ ion of the $HC_2H_3O_2$ and thus render $SrCrO_4$ more insoluble in accordance with what was said in Note **11** above.

* * *

15. The precipitation is conducted in hot solution, the reagent being added a little at a time to prevent the precipitate from coming down in too finely divided form (see Note **9** above). Any local precipitation (generally at the top of the solution) may be due to a high local concentration of C_2H_5OH, causing precipitation of ammonium salts, etc.

* * *

16. In cold solutions of approximately 30 per cent C_2H_5OH by volume only a rather large quantity of Ca will give a precipitate as $CaCrO_4$, whereas traces of Sr will give a precipitate if the procedure has been closely followed.

* * *

17. The confirmatory test for Sr is always made because any $BaCrO_4$ which may not have been removed, if the solution in which Ba was precipitated was too acid, will come down at this point, when the solution is made alkaline and C_2H_5OH added. In addition there is the fact that some $CaCrO_4$ may have been precipitated if the amounts present are large.

* * *

18. $SrCrO_4$ is distinctly soluble in hot water.

19. $BaSO_4$ and $SrSO_4$ will be precipitated by the addition of $(NH_4)_2SO_4$, but not Ca, under these conditions. $SrSO_4$ is soluble in hot HCl, whereas $BaSO_4$ is only slightly so. The solubility of each is due to the formation of the moderately weakly dissociated HSO_4^- ion, the bisulphates of Ba and Sr being much more soluble than the sulphates:

$$H^+ + SO_4^- \rightleftarrows HSO_4^-.$$

* * *

20. The quantity of $(NH_4)_2C_2O_4$ recommended is sufficient to give a precipitate with even traces of Ca, but will not precipitate MgC_2O_4 unless Mg is present in large quantity. After the presence of Ca has been established, more $(NH_4)_2C_2O_4$ is added to completely precipitate the Ca with the possibility of precipitating a small amount of MgC_2O_4. Since the presence of Ca has already been detected, this does not interfere.

* * *

21. The precipitation of CaC_2O_4 is hindered by the fact that MgC_2O_4 is weakly ionized and thus prevents the $C_2O_4^-$ ion from reacting with the Ca. After an amount of this ion equivalent to all the Mg present has been added, CaC_2O_4 begins to precipitate.

* * *

22. If the solution is filtered from the CaC_2O_4 within a short time after the second portion of $(NH_4)_2C_2O_4$ has been added, the possibility that the precipitate contains MgC_2O_4 is minimized, since the latter has an unusual tendency to form supersaturated solutions and therefore does not precipitate readily.

* * *

23. Because of faulty procedure, any Sr not precipitated in its proper place might come down with Ca as SrC_2O_4, since the latter is not a great deal more soluble than CaC_2O_4. The possibility of MgC_2O_4 precipitating has already been spoken of. For these reasons it is always advisable to make the confirmatory test for Ca.

This confirmatory test depends upon the fact that CaC_2O_4 dissolves to a slight extent in H_2SO_4 as a result of the formation of the weaker oxalic acid (see *Theory*, p. 159). This small quantity of $CaSO_4$ is reprecipitated by the addition of more alcohol. Any $MgSO_4$ which has been dissolved will not come down under these conditions, since it is too soluble. SrC_2O_4 is not soluble to any appreciable extent in the mixture of C_2H_5OH and H_2SO_4 first added, and therefore does not interfere.

* * *

24. This solution is made strongly ammoniacal to prevent the hydrolysis of $MgNH_4PO_4$, which would increase its solubility.

$$Mg^{++} + NH_4^+ + PO_4^{\equiv} + H^+ + OH^- \rightleftarrows Mg^{++} + NH_4OH + HPO_4^{=}.$$

Increasing the concentration of the NH_4OH tends to reverse the hydrolysis and minimize the formation of the $HPO_4^{=}$ ion.

* * *

25. If the precipitate for Mg is not crystalline, it may be due to Sr or Ca phosphates formed from incomplete removal of these two elements. In this case the Mg should be confirmed. To do this, treat the $MgNH_4PO_4$ with 3 c.c. of dilute H_2SO_4, and add 6 c.c. of C_2H_5OH to the filtrate so obtained. Shake the mixture for several minutes and filter from any precipitate. Make the filtrate strongly alkaline with conc. NH_4OH (about 5 c.c.) and then add 5 c.c. Na_2HPO_4 and allow to stand for half an hour. A white precipitate confirms the presence of Mg and is again $MgNH_4PO_4$. By dissolving the phosphates of Sr, Ca, and Mg in H_2SO_4 and then adding C_2H_5OH, the former two are completely precipitated as sulphates and only Mg remains in the solution.

The reaction for the formation of $MgNH_4PO_4$ is as follows:

$$Mg(C_2H_3O_2)_2 + Na_2HPO_4 + NH_4OH \rightarrow MgNH_4PO_4 + 2NaC_2H_3O_2 + H_2O.$$

SUMMARY OF GROUP 4

The principles of separation applied in this group are:

1. (Of Group 4 from Group 5) that the carbonates of Group 4 are insoluble in alkaline alcoholic solutions in the presence of NH_4 salts.

2. (Of Ba from Sr, Ca, and Mg) that $BaCrO_4$ is insoluble in weakly acid solution in the presence of NH_4 salts.

3. (Of Sr from Ca and Mg) that $SrCrO_4$ is insoluble in ammoniacal alcoholic solutions.

4. (Of Ca from Mg) that CaC_2O_4 is insoluble in ammoniacal solutions.

Equations on Group 4 Metals

BARIUM

1. Barium nitrate and ammonium carbonate.
2. Barium carbonate and acetic acid.
3. Barium acetate and potassium chromate.
4. Barium chromate and hydrochloric acid.
5. Barium chloride and flame.

STRONTIUM

1. Strontium nitrate and ammonium carbonate.
2. Strontium carbonate and acetic acid.
3. Strontium acetate and potassium chromate (in weak acid solution).
4. Strontium acetate and potassium chromate (in alkaline alcoholic solution).
5. Strontium acetate and hot water.
6. Strontium acetate and ammonium sulphate.
7. Strontium sulphate and hydrochloric acid (hot).
8. Strontium chloride and flame.

CALCIUM

1. Calcium nitrate and ammonium carbonate.
2. Calcium carbonate and acetic acid.
3. Calcium acetate and potassium chromate (in weak acid solution).
4. Calcium acetate and potassium chromate (in alkaline alcoholic solution).
5. Calcium acetate and ammonium oxalate.
6. Calcium oxalate and sulphuric acid.
7. Calcium sulphate and alcohol (not a reaction).

MAGNESIUM

1. Magnesium nitrate and ammonium carbonate (in the presence of alcohol).
2. Magnesium ammonium carbonate and acetic acid.
3. Magnesium acetate and potassium chromate (in weak acid solution).
4. Magnesium acetate and potassium chromate (in alkaline alcoholic solution).
5. Magnesium acetate and ammonium oxalate.
6. Magnesium acetate, ammonium hydroxide, and sodium hydrogen phosphate.
7. Magnesium ammonium phosphate and sulphuric acid.
8. Magnesium sulphate, ammonium hydroxide, and sodium hydrogen phosphate.

Questions on Group 4 Metals

(See also *Theory*, pp. 168–174.)

1. If the ammoniacal solution at the beginning of Group 3 were allowed to stand for a long time in the air, what effect might this have on Group 4 metals?
2. Would NH_4HCO_3 be just as satisfactory for the precipitation of Group 4 as $(NH_4)_2CO_3$?
3. Why is the solution of $(NH_4)_2CO_3$ made strongly alkaline with NH_4OH at the beginning of Group 4?

4. Why is the precipitation of Group 4 carried out in a cold solution and allowed to stand for a considerable time before filtering?
5. Does alcohol have any chemical part in the precipitation of Group 4? Explain its use.
6. What is the purpose of evaporating away the acetic acid (added to dissolve the carbonates of Group 4) and then adding more acetic acid before testing for Ba?
7. Under what conditions is the confirmatory test for Ba advisable?
8. What is the basis of the separation of Ba from the other members of Group 4 metals?
9. Why is $BaCrO_4$ more readily soluble in HCl than in $HC_2H_3O_2$?
10. Why is NH_4OH added before making the test for Sr? Why alcohol?
11. Why is Sr precipitated as $SrSO_4$ and the latter dissolved in HCl before the confirmatory test, when $SrCrO_4$ has already been dissolved in water and thus gives a solution from which the flame test might be made?
12. Why is the confirmatory test for Sr always necessary, especially when Ba is present?
13. Explain why $SrSO_4$ is soluble in HCl.
14. Why are flame tests made from solutions of the chlorides wherever this is possible?
15. What is the effect of the presence of Mg upon the precipitation of Ca as oxalate?
16. It is possible to add $(NH_4)_2C_2O_4$ to a solution of a Mg salt in quantity sufficient to cause precipitation of MgC_2O_4 and yet not get a precipitate for several minutes. Explain.
17. Explain the confirmatory test for Ca.
18. Why is the solution from which Mg is precipitated as $MgNH_4PO_4$ made strongly alkaline with NH_4OH?
19. Why is the confirmatory test for Mg sometimes necessary even though there are no other elements tested for in this group after the removal of Mg?
20. Explain the confirmatory test for Mg.
21. What compound of similar character might be added, in making the confirmatory test for Mg, in place of Na_2HPO_4?

TABLE 8

GROUP 5 METALS

(*Na, K, NH_4*)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Sol. 1 (Table 7)	Evap. HCl	White residue	Group 5 present	NaCl, HCl	X
2.	Res. 1	Evap. HCl, H_2O	Solution	X	X	NaCl, KCl
3.	Sol. 2 (part)	$Na_3Co(NO_2)_6$	Yellow ppt.	K pres.	$K_2NaCo(NO_2)_6$	$Na_3Co(NO_2)_6$
4.	Ppt. 3	HCl, Flame screen	Violet flame	K conf.	X	X
5.	Sol. 2 (rest)	K_2HSbO_4	White ppt.	Na pres.	Na_2HSbO_4	X
6.	Ppt. 5	HCl, Flame	Yellow flame	Na conf.	X	X
7.	Orig. subst.	NaOH, K_2HgI_4	Orange ppt.	NH_4 pres.	$HgO.Hg(NH_2)I$	X

ANALYSIS OF THE ALKALI GROUP (GROUP 5)

(*Na, K, NH_4*)

Definition. — Those metallic radicals whose chlorides, sulphides, hydroxides and carbonates are soluble under the conditions laid down in the previous groups.

(33) Elimination of Ammonium Salts. — Evaporate the filtrate from (**28**) (or the last group analyzed), which contains sodium, potassium, and ammonium salts, to dryness, and ignite ① over a free flame. Care should be taken to see that the dish is heated on all sides until all signs of white fumes have ceased to come off; then heat for five minutes more; at the same time do not allow the dish to become red-hot ②. After cooling add 3 c.c. of conc. HCl and repeat ③ the evaporation and ignition ④. If a white residue ⑤ ⑥ remains, it may consist of NaCl and KCl. After cooling, dissolve the residue in 3 c.c. of water ⑦ and filter, taking care to pour the solution through the point of the filter so that too much will not be lost. Treat one-third of this solution by (**34**) for K and the other two-thirds by (**35**) for Na.

(34) Detection of Potassium. — Dilute the 1 c.c. portion of the filtrate from (**33**) to 3 c.c. and add 3 c.c. of $Na_3Co(NO_2)_6$. Let the mixture stand for at least fifteen minutes unless a precipitate forms sooner ⑧. Filter and wash thoroughly with cold H_2O. A yellow precipitate ⑨ indicates the presence of **Potassium** and is $K_2NaCo(NO_2)_6$. Dissolve the precipitate in a 5 c.c. portion of hot HCl⑩, evaporate the solution to 1 c.c., and apply the flame test

with a clean platinum wire and a celluloid screen, or cobalt glass ⑪ thick enough to absorb any yellow light from Na. A violet flame confirms the presence of K.

(35) Detection of Sodium. — To the remaining portion of the filtrate from **(33)** in a test-tube, add an equal volume of KH_2SbO_4 and allow it to stand for an extended period ⑫ of time (twenty-four hours if possible). A white *crystalline* precipitate indicates the presence of **Sodium** and is NaH_2SbO_4, which tends to adhere to the glass. Therefore, if any flocculent precipitate (which is no indication of Na) is formed, shake the mixture, allow it to stand for a few seconds and then decant the liquid and the flocculent precipitate away from the precipitate of NaH_2SbO_4.

Detection of Ammonium. — To 3 c.c. of the original solution ⑬ given for analysis, or 0.2 g. of the original solid, in a small beaker, add enough NaOH ⑭ (2 c.c. in the case of a solid) to make the solution alkaline. Cover the beaker with a dry watch glass on the under side of which has been pasted a small piece of red litmus paper moistened with H_2O. Warm the mixture over a water bath ⑮ for two to three minutes. If the red litmus turns blue it indicates the presence of the **Ammonium Radical.**

If the ammonium radical is present and it is desired to estimate its quantity, place a sample, similar to the one used above, in a small flask, add the same quantity of NaOH as above, and dilute to 15 c.c. Stopper this flask tightly with a rubber stopper fitted with a delivery tube about 10 inches in length. Slowly distil the mixture in the flask into the bottom of a test-tube submerged in cold water, until about half the mixture has been distilled over. To this solution add K_2HgI_4 ⑯ a drop at a time, until precipitation is complete. A brown or orange precipitate confirms the presence of the **Ammonium Radical** and is $HgO.Hg(NH)_2I$.

NOTES ON THE DETECTION OF THE ALKALI GROUP

(*Group 5*)

1. All ammonium salts are decomposed by high temperatures and may therefore be removed by ignition. This must be done with great care since NH_4 salts give a precipitate with the $Na_3Co(NO_2)_6$ reagent for K, which cannot be distinguished by ordinary inspection from the precipitate with K salts. It is for this reason that the evaporation and ignition are repeated.

* * *

2. The temperature of ignition should not be raised to a red heat since KCl and NaCl are somewhat volatile at such a temperature.

* * *

3. If large amounts of Na and K, particularly the latter, are present, it is advisable to use only part of the residue for the subsequent tests. In the event that the residue is large, warm it thoroughly with 5 c.c. of HCl and stir with a glass rod. Pour off this liquid from any undissolved residue and repeat the operation with 2 c.c. of conc. HCl, adding the second solution to the first. The combined solutions are evaporated and treated as directed in the regular procedure.

   In this way only a limited portion of the Na and K salts present are dissolved. This increases the delicacy of the Na test particularly, since the presence of large amounts of K salts reduced the sensitivity of the latter considerably.

* * *

4. Unless the dish appears to be entirely unstained by any residue the tests for Na and K should be carried through. A dry residue which to the eye may appear rather small may represent an appreciable quantity of Na and K salts. It is better to err on the safe side in deciding whether or not there is a residue present in this case.

5. As result of small amounts of dust, impurities in NH_4 salts added, decomposition of alcohol, filter paper fibers, etc., a black or brown residue is often obtained by this ignition. This will not be soluble in the H_2O added and is therefore removed by filtration.

* * *

6. It is advisable to carry out the subsequent test for Na in a concentrated solution. For this reason only a small quantity of H_2O is added at this point to save evaporation later.

* * *

7. With normal amounts of K salts, $Na_3Co(NO_2)_6$ gives a precipitate readily, but in traces this precipitate forms rather slowly and solution should be allowed to stand.

* * *

8. Since the color of the $Na_3Co(NO_2)_6$ solution is not very different from the precipitate of $K_2NaCo(NO_2)_6$, it is better to look for the latter on the filter after the reagent has been washed away.

* * *

9. The precipitate for K should always be confirmed because of the possibility that the ammonium salts may not have been completely removed by ignition. Traces of NH_4 salts will give a precipitate similar to that of K (see Note **1** above). The composition of the precipitate is $(NH_4)_2NaCo(NO_2)_6$.

* * *

10. $K_2NaCo(NO_2)_6$ is dissolved in HCl as a result of the formation of the weakly ionized unstable HNO_2 (see *Theory*, p. 117 *et seq.*), according to the following reactions:

$$K_2NaCo(NO_2)_6 + 6HCl \rightarrow 2KCl + NaCl + CoCl_3 + 6HNO_2.$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O.$$

The solution is evaporated so that the pale violet of the potassium flame may be more easily seen, especially when the amounts of K are small.

11. The celluloid screen or cobalt glass is used to absorb any yellow light emitted when Na is present. The Na flame is much stronger than that of K and would obscure the latter even if Na is present in only small amounts. If cobalt glass is used, it may be found necessary to use more than one thickness of the kind which is ordinarily supplied. In any event, the student should try this test on a known solution before proceeding with the analysis of unknowns.

* * *

12. The precipitation of NaH_2SbO_4 takes place very slowly, particularly when the amounts of Na present are small. It is characterized by the tenacity with which the precipitate adheres to the walls of the vessel in which it is precipitated, often requiring acid to remove it by solution. It forms relatively large granular crystals.

The student must be careful to distinguish the precipitate of NaH_2SbO_4 from any small amount of a flocculent precipitate which may form in this test. Small quantities of the alkaline earths or other elements, not completely removed, may give a precipitate with the KH_2SbO_4 which is flocculent. The KH_2SbO_4 itself tends to decompose slowly, precipitating H_3SbO_4 which is also a flocculent white precipitate. Any such precipitates can be readily decanted from the NaH_2SbO_4 because of the tendency of the latter to adhere to the glass,

* * *

13. The original unknown, either solution or solid, received by the student, should be tested for NH_4, because ammonium salts are being added at different points throughout the regular procedure. It would not do, for example, to use any of the filtrate from the alkaline earth group to test for NH_4, since NH_4OH and $(NH_4)_2CO_3$ have just been added. To avoid confusion to beginners on this point, it is well to make the NH_4 test as soon as the sample of the unknown is received.

14. Weakly ionized, unstable NH_4OH is formed when NaOH is added to an ammonium salt (see *Theory*, p. 117 *et seq.*). When the solution is warmed, NH_3 is evolved and, coming in contact with the moist litmus, forms small amounts of NH_4OH, thus giving the test:

$$NH_4Cl + NaOH \rightarrow NaCl + NH_4OH.$$
$$NH_4OH \rightarrow NH_3 + H_2O.$$
$$NH_3 + H_2O \text{ (on litmus)} \rightarrow NH_4OH.$$

Care should be taken in this test that the watch glass is dry at the edges where it touches the beaker, and that the NaOH is not poured down the side of the beaker. The latter is liable to reach the litmus by capillary attraction and thus give misleading results.

* * *

15. The water bath and not a free flame is used to warm the solution because the latter might boil, over the free flame, and thus cause spattering of the NaOH solution onto the litmus paper. Since any solution of a solid in water boils at a higher temperature than water itself, the NaOH solution will not boil on the water bath.

The solution should not be heated for more than two to three minutes since NH_3 fumes in the laboratory may be sufficient to turn the paper slightly, over a longer period of time.

* * *

16. An alkaline solution of K_2HgI_4, the so-called Nessler reagent, is a very sensitive test for the presence of NH_3. The reaction which takes place is as follows:

$$2K_2HgI_4 + 4NH_4OH \rightarrow HgO.Hg(NH_2)I + 3H_2O + 4KI + 3NH_4I$$

A distinct orange or brown precipitate is produced if there is as little as 0.2 mg. of NH_4 present. A pronounced yellow color is obtained with much smaller quantities. Therefore, unless a distinct precipitate is formed, NH_4 is present in traces only, and these may be due to impurities in the water used.

SUMMARY OF GROUP 5

The principles of separation applied in this group are:

1. (Of NH_4 salts from Na and K) that NH_4 salts are volatilized under moderate ignition.

2. (Of K from Na) that $K_2NaCo(NO_2)_6$ is precipitated by the addition of the soluble $Na_3Co(NO_2)_6$, in weakly acid solution.

3. (Of Na from K) that NaH_2SbO_4 is precipitated in alkaline solution by the soluble KH_2SbO_4.

4. (Of NH_4 from the rest of the elements) that NH_4OH is a weak base and decomposed under gentle warming.

Equations on Group 5 Metals

SODIUM

1. Sodium nitrate and heat (ignition).
2. Sodium nitrite and hydrochloric acid.
3. Sodium chloride and sodium cobaltinitrite.
4. Sodium chloride and potassium antimonate.
5. Primary sodium antimonate and hydrochloric acid.
6. Sodium chloride and flame.

POTASSIUM

1. Potassium nitrate and heat (ignition).
2. Potassium nitrite and hydrochloric acid.
3. Potassium chloride and sodium cobaltinitrite.
4. Potassium sodium cobaltinitrite and hydrochloric acid.
5. Potassium chloride and flame.

AMMONIUM

1. Ammonium nitrate and sodium hydroxide heated (water bath).
2. Ammonia and water (litmus paper).
3. Ammonium hydroxide and litmus paper (not a reaction).
4. Ammonium hydroxide and potassium mercuri-iodide.

Questions on Group 5 Metals

(See also *Theory*, pp. 168–174.)

1. Write reactions for the decomposition of the following ammonium salts by heat: NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, $NH_4C_2H_3O_2$, $(NH_4)_2C_2O_4$.
2. Why is the evaporation and ignition of the beginning of Group 5 repeated?
3. Why is the residue dissolved both times in HCl instead of HNO_3 or H_2SO_4?
4. Account for the fact that the residue on ignition of Group 5 is sometimes black, or dark brown.
5. Explain why the vapors catch fire frequently in the evaporation of Group 5.
6. Why should the residue in Group 5 not be too strongly ignited?
7. Name all the common compounds of potassium and sodium which are insoluble in water in the ordinary sense of the term. Write their formulas.
8. Why is it necessary to make the confirmatory test for K if the precipitate with sodium cobaltinitrite is small? Why is a screen used in the confirmatory test for K?
9. To what sources might a flocculent white precipitate in the test for Na be due? What is the nature of the precipitate for Na?
10. Explain why NaH_2SbO_4 is soluble in strong acids.
11. Devise a confirmatory test for Na.
12. Why is the test for NH_4 always made on the original material?
13. Could $Ca(OH)_2$, $Ba(OH)_2$ or KOH be used in the test for NH_4 instead of NaOH? Upon what two properties of NH_4OH does the test depend?
14. Why should the litmus test for NH_4 not be allowed to stand too long before deciding on a color change?

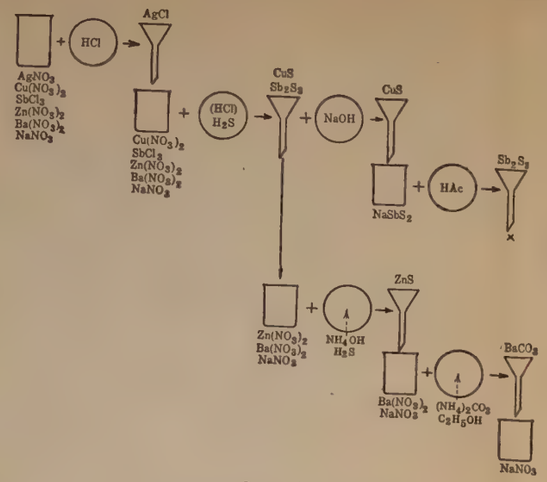


CHART 1
GROUP SEPARATION (PRELIMINARY)

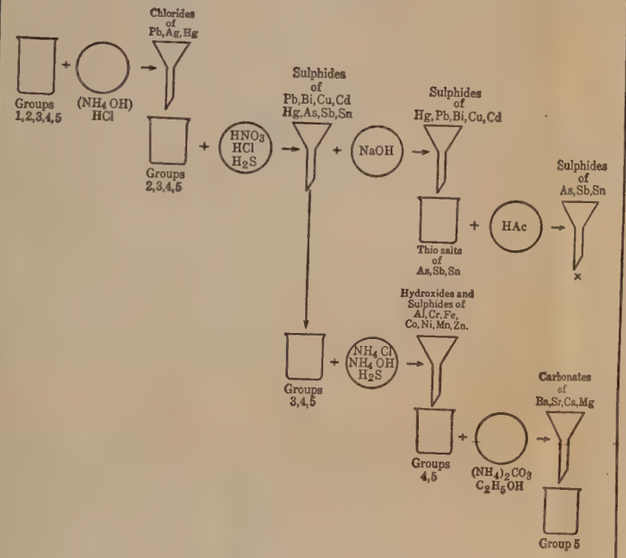
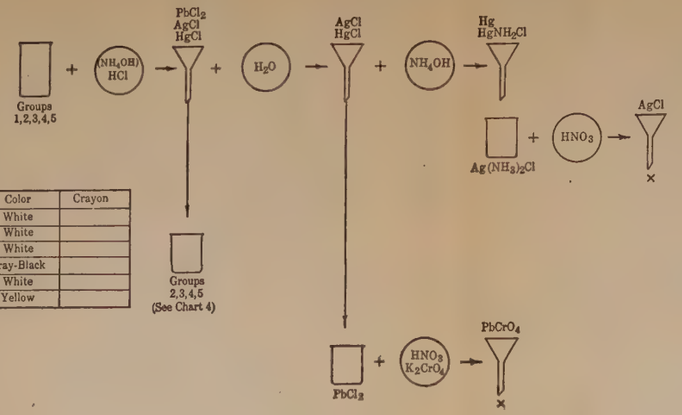
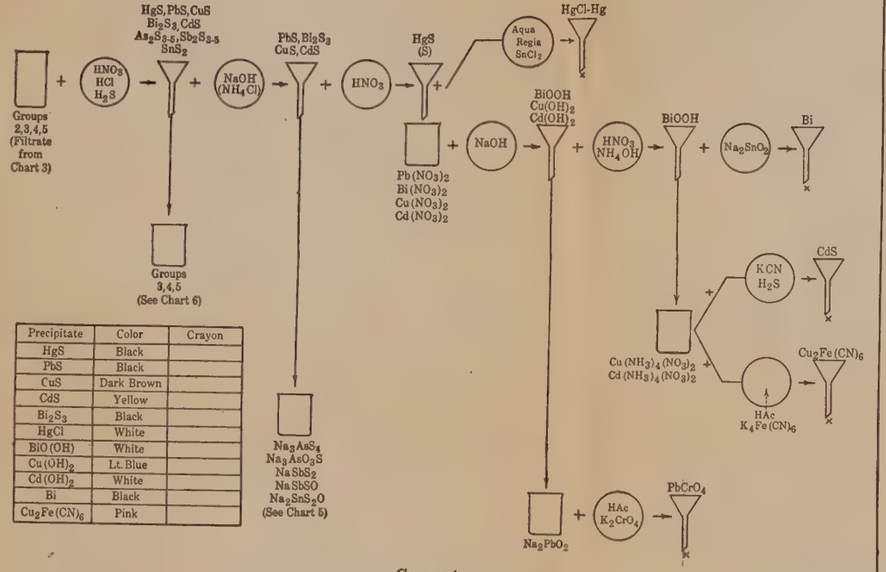


CHART 2
GROUP SEPARATIONS



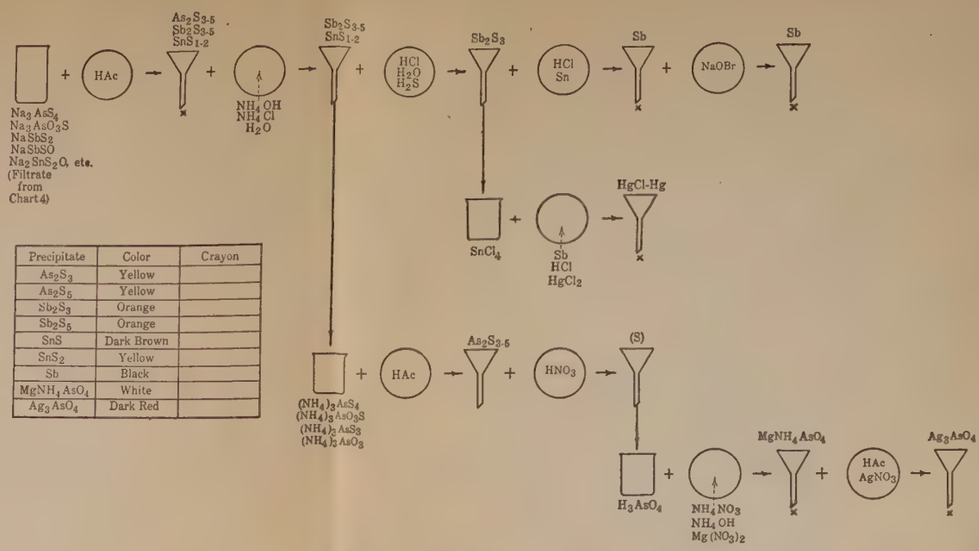
Precipitate	Color	Crayon
$PbCl_2$	White	
AgCl	White	
HgCl	White	
Hg	Gray-Black	
$HgNH_2Cl$	White	
$PbCrO_4$	Yellow	

CHART 3
GROUP 1 METALS



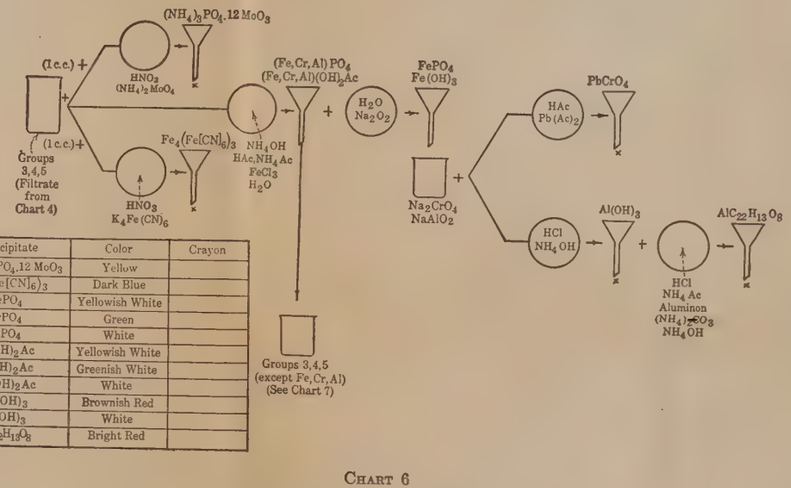
Precipitate	Color	Crayon
HgS	Black	
PbS	Black	
CuS	Dark Brown	
CdS	Yellow	
Bi_2S_3	Black	
HgCl	White	
BiO(OH)	White	
$Cu(OH)_2$	Lt. Blue	
$Cd(OH)_2$	White	
Bi	Black	
$Cu_2Fe(CN)_6$	Pink	

CHART 4
GROUP 2A METALS



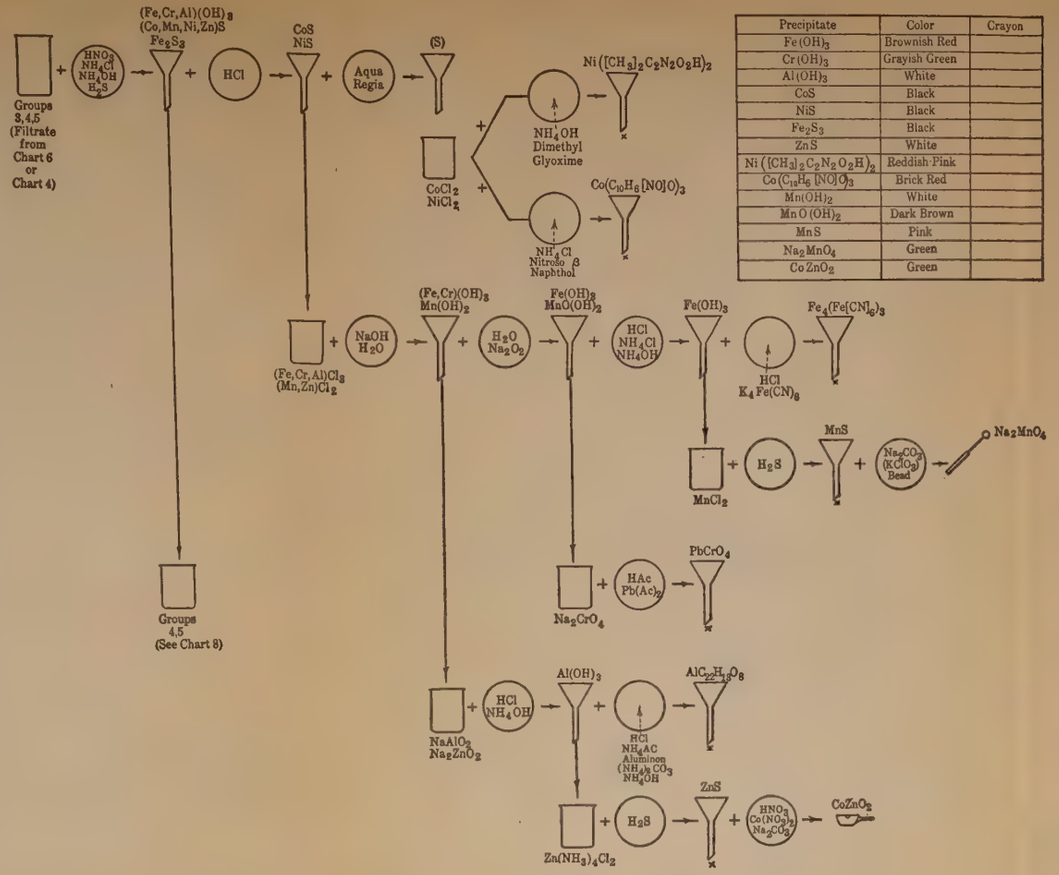
Precipitate	Color	Crayon
As_2S_3	Yellow	
As_2S_5	Yellow	
Sb_2S_3	Orange	
Sb_2S_5	Orange	
SnS	Dark Brown	
SnS_2	Yellow	
Sb	Black	
$MgNH_4AsO_4$	White	
Ag_3AsO_4	Dark Red	

CHART 5
GROUP 2B METALS



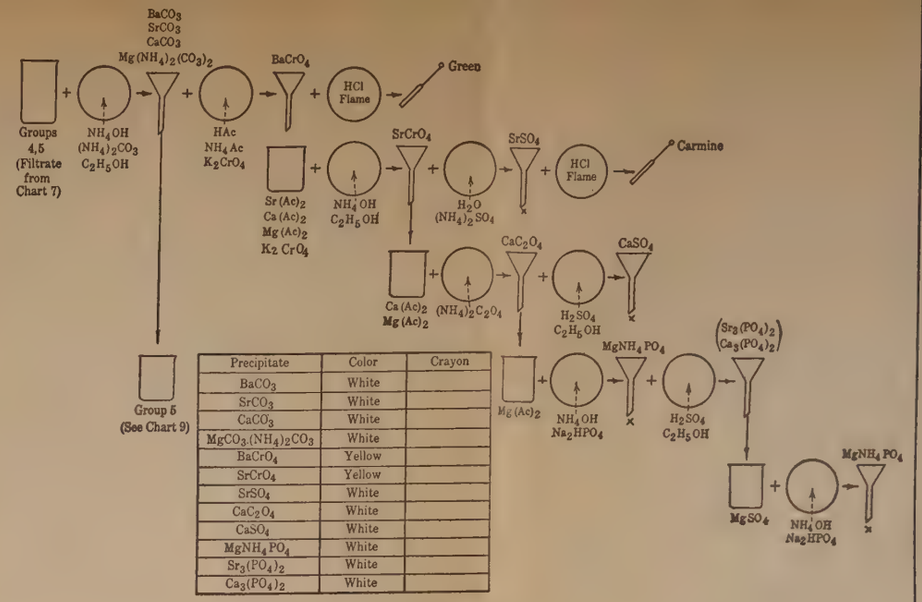
Precipitate	Color	Crayon
$(NH_4)_3PO_4.12\,MoO_3$	Yellow	
$Fe_4(Fe[CN]_6)_3$	Dark Blue	
$FePO_4$	Yellowish White	
$CrPO_4$	Green	
$AlPO_4$	White	
$Fe(OH)_2Ac$	Yellowish White	
$Cr(OH)_2Ac$	Greenish White	
$Al(OH)_2Ac$	White	
$Fe(OH)_3$	Brownish Red	
$Al(OH)_3$	White	
$AlC_{22}H_{13}O_8$	Bright Red	

CHART 6
PHOSPHATE SEPARATION



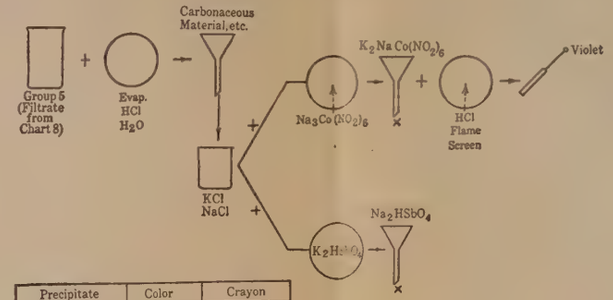
Precipitate	Color	Crayon
$Fe(OH)_3$	Brownish Red	
$Cr(OH)_3$	Grayish Green	
$Al(OH)_3$	White	
CoS	Black	
NiS	Black	
Fe_2S_3	Black	
ZnS	White	
$Ni([CH_3]_2C_2N_2O_2H)_2$	Reddish Pink	
$Co(C_{15}H_6[NO]O)_3$	Brick Red	
$Mn(OH)_2$	White	
$MnO(OH)_2$	Dark Brown	
MnS	Pink	
Na_2MnO_4	Green	
$CoZnO_2$	Green	

CHART 7
GROUP 3 METALS



Precipitate	Color	Crayon
$BaCO_3$	White	
$SrCO_3$	White	
$CaCO_3$	White	
$MgCO_3.(NH_4)_2CO_3$	White	
$BaCrO_4$	Yellow	
$SrCrO_4$	Yellow	
$SrSO_4$	White	
CaC_2O_4	White	
$CaSO_4$	White	
$MgNH_4PO_4$	White	
$Sr_3(PO_4)_2$	White	
$Ca_3(PO_4)_2$	White	

CHART 8
GROUP 4 METALS



Precipitate	Color	Crayon
$K_2NaCo(NO_2)_6$	Yellow	
Na_2HSbO_4	White	

CHART 9
GROUP 5 METALS

ACID RADICAL PROCEDURE — GENERAL DISCUSSION

The detection of the acid radicals is not susceptible to the same sort of systematic procedure as that of the metals. That is to say, no satisfactory method of procedure has been worked out whereby a group of acid radicals may be precipitated out by adding one or two reagents, and this precipitate systematically and eliminatively analyzed for members of the group. It is true that the acid radicals may be classified into groups which are precipitated by certain reagents under certain conditions; but in some cases these subdivisions are not too well defined, and in any event the analysis of such group precipitates is not practical. Thus the sulphides, ferrocyanides and ferricyanides, chlorides, bromides, iodides, and sulphocyanates are all precipitated by silver nitrate in nitric acid solution, but the analysis of such a group precipitate would be attended with difficulties.

Since the primary purpose of an elementary course in qualitative analysis should be to establish scientific systematic reasoning in connection with certain chemical facts, and since the number of acid radicals which occur commonly is fairly small, it is deemed advisable in this work to limit the procedure for acid radicals to those which do occur more commonly, and most of which are amenable to some sort of systematic treatment. The procedure subsequently given provides for the detection of the following acid radicals:

Ferrocyanide	Sulphide	Fluoride
Ferricyanide	Sulphate	Nitrate
Thiocyanate	Sulphite	Nitrite
Iodide	Chromate	Borate
Bromide	Oxalate	Arsenite
Chloride	Carbonate	Arsenate

The detection of silicate and phosphate has been provided for previously.

The procedure for the detection of acid radicals can often be considerably simplified in several ways. A knowledge of what metals are present in the solution often allows very definite eliminations to be made. Thus if lead or barium be present and the substance is water or acid soluble, there can be no sulphates in the solution; if silver be present and the solution is not ammoniacal, sulphides, ferrocyanides and ferricyanides, iodides, bromides, chlorides and thiocyanates must be absent. By use of the solubility table in the appendix such eliminations can frequently be made. Furthermore, if the original substance is a solution and is acid, nitrites, sulphites, sulphides, and carbonates may be eliminated. Certain radicals which are oxidizing in character cannot exist in the presence of others which are easily oxidized. Thus chromates and arsenates would not be found in the same solution with iodides or sulphites. The presence of oxidizing and reducing agents may be determined by two or three general reagents although the general determination of the presence of oxidizing constituents is attended with uncertainty and is here omitted. Lastly, the presence of certain acid radicals is indicated definitely by the metallic analysis. If chromium and arsenic are not found as metals, then there can be no chromates, arsenites, or arsenates in the solution. By intelligent use of knowledge at hand, it is seldom that the procedure for the detection of acid radicals cannot be considerably simplified.

Special Treatment of Naturally Occurring and High Temperature Products. — Since naturally occurring substances (except natural salt deposits) have in general been formed under geologic conditions involving high temperatures, the number of acid radicals which occur in such products is much smaller than is provided for in the following

procedures. The same is true of many industrial products resulting from high-temperature processes. The reason is that the majority of the acid radicals are decomposed or volatilized at high temperatures and would not be found in products resulting from such. Therefore in testing rocks, ores, and minerals in general, furnace slags, metallurgical products, glasses, ceramic materials, etc., only the following radicals need be tested for: chlorides, fluorides, sulphates, sulphides, borates, phosphates, and silicates (in rare instances, cyanides). Clearly, the procedure for acid radicals can be greatly simplified in the analysis of such products. In fact, the tests for sulphides, carbonates, fluorides, and borates can be made on the original material. The silicates are tested for on the residue from (**64**), while the tests for chlorides, sulphates, and phosphates may be made by direct tests on separate samples of the solution of the original material in HNO_3 or HCl (except chlorides) or H_2SO_4 (except sulphates).

ANALYSIS FOR ACID RADICALS: PRELIMINARY TREATMENT

(36a) Preparation of the Solution. — If the original unknown is a solution prepared in the laboratory, take 25 c.c. of it and add 15 c.c. of Na_2CO_3 solution ①. Boil gently in a covered casserole for ten minutes, replacing any water which may evaporate. Filter and wash the precipitate, which is to be kept ② for treatment by (**60**) in event that subsequent procedures show this to be necessary. Treat portions of the solution as recommended in (**37**), etc.

(36b) If the original is a solution from natural or industrial sources, test it with litmus paper. If it is acid, add NH_4OH until all the acid has been neutralized. Put 10 c.c. of this solution in a weighed dish and evaporate it just to dryness over a water or steam bath. Weigh the dish again and calculate the amount of solid in 10 c.c. of the solution. To an amount of the neutralized solution equivalent to 2 g. of solid add 20 c.c. of Na_2CO_3 and treat as directed above. Bring the solution to a volume of about 40 c.c. either by evaporation or by addition of water, and treat portions of it as directed in (**37**).

(36c) If the original substance is a solid ③ take 2 g. of it and boil with 20 c.c. of Na_2CO_3 as directed above, bringing the solution to 40 c.c. eventually and treating by (**37**).

(37a) Detection of the Chloride Group. — To 1 c.c. of the prepared solution from (**36a, b,** or **c**) or (**64**) add HNO_3 to acid

reaction, and boil the solution until the CO_2 is removed; dilute with a little water and add 2 c.c. of $AgNO_3$ ④. Note the color of any precipitate which forms. A white or colored ⑤ precipitate indicates the presence of the **Chloride Group** and may contain $Ag_4Fe(CN)_6$, $Ag_3Fe(CN)_6$, AgCl, AgCNS, AgBr, and AgI. Discard the precipitate and solution and test another sample of the solution from (**36a, b,** or **c**) by (**38**) for individual members of the chloride group.

(**37b**) **Detection of the Sulphate Group.** — Carefully neutralize 2 c.c. of the solution from (**36a, b,** or **c**) with $HC_2H_3O_2$ and then add a 3 c.c. excess. If a precipitate forms remove it by filtration and discard it. To the filtrate, add 1–2 c.c. of $BaCl_2$ ⑥ and 3–5 c.c. of $CaCl_2$ ⑥ (which must be free of sulphates). Warm the solution gently for several minutes and allow it to stand for at least ten minutes. A white or yellow precipitate indicates the presence of the **Sulphate Group** and may consist of $BaSO_4$, $BaSO_3$, $BaCrO_4$, CaC_2O_4, and CaF_2. Discard the precipitate and solution. Test a sample of the solution from (**36a, b,** or **c**) by (**48**) for the detection of the individual members of this group.

(**37c**) **Detection of Reducing Constituents** ⑦. — Dilute 2 c.c. of the solution from (**36a, b,** or **c**) to 5 c.c. Acidify carefully with HCl and add 2–3 drops of $FeCl_3$ and a like amount of freshly prepared ⑧ $K_3Fe(CN)_6$. Let the mixture stand for several minutes. (A greenish coloration or blue precipitate ⑨ indicates the presence of one or more of the following: **Sulphite, Ferrocyanide, Nitrite, Iodide, and Sulphide.** If no such precipitate ⑩ occurs, the subsequent tests for all these radicals may be omitted. If the test is doubtful, a blank test should be made, using the reagents above with 2 c.c. of pure Na_2CO_3 solution.

NOTES ON PRELIMINARY TREATMENT FOR ACID RADICALS

1. The purpose of boiling the solution or solid with Na_2CO_3 is to replace most of the metallic ions in the unknown by the sodium ion. This accomplishes two things. It removes from solution, ions of the heavier metals which might interfere with the acid radical detection, and, in the case of insoluble solids, replaces the metallic radical by sodium and thereby brings the acid radical into the solution in the form of a soluble sodium salt. These things are accomplished as follows: Na_2CO_3 is a salt of a weak base and a strong acid. It is therefore hydrolyzed in solution (see *Theory*, p. 130 *et seq.*) and supplies both OH^- and $CO_3^=$ ions. Since the hydroxides, carbonates, or basic carbonates of all the metals except Na, K, and NH_4 are insoluble (some of the amphoteric metals are not completely precipitated) boiling with Na_2CO_3 removes all the metallic radicals except those of Group 5 in one step. In the case of an insoluble solid, $BaSO_4$ for example, boiling with Na_2CO_3 forms $BaCO_3$ and Na_2SO_4 by metathesis. In this way the $SO_4^=$ radical is brought into soluble form and the Ba is removed. The extent to which this happens is discussed in Note **3** below.

It is desirable to remove the so-called heavy metals (those with a density greater than 5) because they may either produce precipitates or cause colors which would interfere with the tests for the acid radicals. Thus, upon addition of $BaCl_2$ and $CaCl_2$ in testing for the Group 2 acid radicals, precipitates of AgCl and HgCl would be produced if Ag or monovalent Hg were present. In tests which depend upon the detection of color, such as the borate test, the presence of such ions as impart color to the solution would interfere, as, for example, Cu and Cr.

Of course, if the metallic ion analysis shows that the metals of the first four groups are absent, the treatment with Na_2CO_3 is unnecessary.

Since small amounts of NaOH are formed by the

hydrolysis of Na_2CO_3 (see *Theory*, p. 130), those metals which form amphoteric hydroxides (Sb, Sn, Cu, Al, and Cr) are not completely removed by this treatment; but the amounts which remain in solution do not interfere. Similarly those metals or metalloids which form well-defined acid radicals, such as chromates, arsenates, and arsenites, will not be removed by Na_2CO_3.

* * *

2. The residue from the treatment with Na_2CO_3 is preserved to be tested for the presence of sulphides by (**60**) if not detected by (**38**). This is because many sulphides are not decomposed by boiling with Na_2CO_3. (See Note **1**, p. 191, detection of S and CO_3.)

* * *

3. The degree of conversion of an insoluble compound to its soluble sodium salt depends upon the insolubility of the compound as compared to the insolubility of its carbonate. Consider an insoluble compound AX reacting with Na_2CO_3:

$$AX + Na_2CO_3 \rightarrow Na_2X + ACO_3.$$

Let K_{ax} and K_{ac} represent respectively the solubility products of the original insoluble compound and its corresponding insoluble carbonate. We may then say,

$$[A] \times [X] = K_{ax} \qquad \text{and } [A] \times [CO_3] = K_{ac}.$$

Dividing one by the other, we have,

$$\frac{[X]}{[CO_3]} = \frac{K_{ax}}{K_{ac}}.$$

Since this equation must be satisfied when equilibrium is established, it appears that the concentration of the $X^=$ ion — i.e., the degree to which AX will be decomposed — will depend in part on the relative values of the solubility products of AX and ACO_3 and also on the concentration of the $CO_3^=$ (from Na_2CO_3) ion in the solution.

Let us consider the degree to which the two common insoluble sulphates, $PbSO_4$ and $BaSO_4$, are metathesized by Na_2CO_3. Granted that equilibrium is established at room temperature — this is not strictly true, but is so nearly true that the values are of the same order — the ratio of the solubility products $PbSO_4/PbCO_3 = 1 \times 10^{-8}/3.3 \times 10^{-14} = 303{,}000$. Since the ratio SO_4/CO_3 must have the same value, it is obvious that the conversion of $PbSO_4$ to $PbCO_3$ is complete even though the concentration of $CO_3^=$ ion be very small. In the case of $BaSO_4$, it is quite different because the difference in solubilities of $BaSO_4$ and $BaCO_3$, and therefore the difference in their respective solubility products, is not nearly so great. The ratio of the solubility products is $BaSO_4/BaCO_3 = 1.08 \times 10^{-10}/8.1 \times 10^{-9} = .0133$. From this it is clear, since $SO_4^=/CO_3^= = .0133$, that it is distinctly desirable to have a high concentration of $CO_3^=$ in the solution. Even if the Na_2CO_3 were sufficiently concentrated to give a mixture which is 6M with respect to $CO_3^=$ ion after equilibrium is established, the concentration of the $SO_4^=$ ion would be only $(6 \times .0133 = .0798)$. Even with this small concentration of $SO_4^=$ ion, however, sulphates are easily detected, since $BaSO_4$ is quite insoluble.

* * *

4. As was previously stated, the silver salts of this group of acid radicals are insoluble in dilute solutions of HNO_3.

* * *

5. The color of this group precipitate frequently gives a helpful hint as to what radicals are present. The colors of the precipitates are as follows: AgCl, white; AgCNS, white; Ag_2S, black; AgBr, yellowish white; AgI, bright yellow; $Ag_3Fe(CN)_6$, orange, and $Ag_4Fe(CN)_6$, white.

* * *

6. In weakly acid solutions, $BaSO_4$, $BaSO_3$, and $BaCrO_4$ are insoluble. BaC_2O_4 and BaF_2 are also somewhat insoluble in a weakly acid solution, but the calcium salts

are much more so. For this reason, both $BaCl_2$ and $CaCl_2$ are added to a solution acid with $HC_2H_3O_2$ to determine the presence of the sulphate group. Even under these conditions the precipitate may be small since, with the exception of $BaSO_4$, all of these are salts of weak or fairly weak acids upon which acetic acid would have some solvent effect (see *Theory*, p. 116). For this reason a small precipitate or even turbidity should be interpreted as indicating the presence of the group. The precipitation must be made in a solution which is sufficiently acid, however, since the Ba salts of arsenate, arsenite, phosphate, and borate might be precipitated if the solution were practically neutral.

It should be remembered that in neutralizing the Na_2CO_3 with $HC_2H_3O_2$, some $NaC_2H_3O_2$ is formed which helps to reduce the acidity of the solution by common-ion effect (see *Theory*, p. 102).

* * *

7. $K_3Fe(CN)_6$ is affected by light, and very easily reduced. It should be prepared fresh at frequent intervals. Since it is reduced to ferrocyanide, the addition of $FeCl_3$ would give an immediate precipitate of $Fe_4(Fe[CN]_6)_3$ and thus vitiate the test for reducing agents.

A general test for oxidizing agents such as nitrites, nitrates, and ferricyanides similar to the one for reducing agents, might be made at this point. The test depends on the fact that $MnCl_2$, which is practically colorless, is converted in strong acid solution to dark $MnCl_3$ by oxidizing agents. The test is not always decisive, partly on account of difficulty in detecting a slight darkening and partly on account of the counteracting effect of reducing agents present in the solution. For these reasons it is omitted here.

* * *

8. The detection of reducing agents depends upon the fact that $K_3Fe(CN)_6$ is a powerful oxidizing agent and is therefore easily reduced to $K_4Fe(CN)_6$ (see equations

below). $K_3Fe(CN)_6$ with a ferric salt gives no precipitate, but $K_4Fe(CN)_6$ gives the very insoluble deep blue precipitate of $Fe_4(Fe[CN]_6)_3$. Ferrocyanides already present would, of course, do the same thing.

It might seem that the presence of powerful oxidizing agents would prevent the reduction of the ferricyanide and thus make the test uncertain, but any oxidizing agent sufficiently strong to prevent this test could not exist for any length of time in the presence of such reducing agents as would give the test, even though the original substance were a solid. A negative test, therefore, indicates that the reducing agents enumerated above must be absent.

Along this same line, it may be said that eliminations can also be made with regard to the existence of certain oxidizing agents and reducing agents in the presence of one another. Thus if a solution contains chromates, arsenates, or ferric iron, sulphites and iodides will not be found. Ferricyanides are reduced to ferrocyanides by most reducing agents. Chromates are reduced by Sn^{++} and Fe^{++} as well as by $AsO_3^{=}$ and $S^{=}$, etc.

The reactions which take place in the test for reducing agents are as follows:

(a) $2K_3Fe(CN)_6 + K_2S \rightarrow 2K_4Fe(CN)_6 + S.$

(b) $2K_3Fe(CN)_6 + 2KI \rightarrow 2K_4Fe(CN)_6 + I_2.$

(c) $4K_3Fe(CN)_6 + 2NaSO_3 + 2H_2O \rightarrow 3K_4Fe(CN)_6 + Na_4Fe(CN)_6 + 2H_2SO_4.$

(d) $4K_3Fe(CN)_6 + 4NaNO_2 + 2H_2O \rightarrow 3K_4Fe(CN)_6 + Na_4Fe(CN)_6 + 4HNO_3.$

Questions on General Procedure for Acid Radicals

(See also *Theory*, pp. 168–174.)

1. Why is the original solution prepared with Na_2CO_3 before testing for the acid radicals?
2. Is the removal of all metallic radicals complete when the original material is treated with Na_2CO_3? In what cases may it be incomplete? Explain how this may occur.

3. Give the formula (approximate if necessary) for the precipitate formed by each of the metallic ions with Na_2CO_3. (See the tables on pp. 222 *et seq.*)
4. Explain the dual function of Na_2CO_3 in removing the cations.
5. If the original material is an acid solution, what acid radicals are likely to be absent?
6. If the original solution is basic with NaOH, what ions are likely to be absent?
7. Name the acid radicals which cannot exist for any extended period of time in the presence of one another.
8. Why is the ferricyanide radical used as the test for all reducing agents?
9. Explain in detail exactly how ferricyanides function in the detection of reducing constituents.
10. How might the presence of oxidizing agents be detected by a general reaction?

TABLE 9

GROUP 1 ACID RADICALS

(S, Fe[CN]$_6^{IV}$, Fe[CN]$_6^{III}$, Cl, CNS, Br, I)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Sol. for cations	Na_2CO_3	Colored ppt.	Metals removed	Hydroxides and carbonates of the heavy metals	Sodium salts of the acid radicals
2.	Sol. 1 (2 c.c.)	HCl, $FeCl_3$, $K_3Fe(CN)_6$	Blue ppt.	Reducing agents present	$Fe_4(Fe(CN)_6)_3$	X
3.	Sol. 1 (1 c.c.)	HNO_3, $AgNO_3$	Colored ppt.	Group 1 acids pres.	$Ag_3Fe(CN)_6$, AgCl, $Ag_4Fe(CN)_6$, AgBr, AgI, Ag_2S, AgCNS	X
4.	Sol. 1 (1 c.c.)	$Pb(NO_3)_2$	Black ppt.	Sulphides pres.	PbS	X
5.	Sol. 1 (4 c.c.)	$HC_2H_3O_2$, $Ni(NO_3)_2$	Colored ppt.	$Fe(CN)_6^{IV}$ $Fe(CN)_6^{III}$ present	$Ni_2Fe(CN)_6$, $Ni_3(Fe(CN)_6)_2$	X

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
6.	Sol. 1 (10 c.c.)	HNO_3, $(NH_4)_2MoO_4$	Red ppt.	$Fe(CN)_6^{IV}$ present	$Na_2(MoO_2.Fe(CN)_6.2MoO_3.20H_2O$	$Na_3Fe(CN)_6$, NaCl, NaBr, NaI, NaCNS
7.	Sol. 6	NH_4OH, Na_2SO_3, $HC_2H_3O_2$, $(NH_4)_2MoO_4$	Red ppt.	$Fe(CN)_6^{III}$ present	Same as ppt. 6	NaCl, NaBr, NaI, NaCNS
8.	Sol. 7	HNO_3, $AgNO_3$	Colored ppt.	Cl, Br, I, CNS present	AgCl, AgBr, AgI, AgCNS	X
9.	Ppt. 8	NH_4OH, NH_4NO_3, $AgNO_3$	Partial solution	Cl diss.	(AgCl), AgBr, AgI, AgCNS	$Ag(NH_3)Cl$
10.	Sol. 9	HNO_3	White ppt.	Cl pres	AgCl	
11.	Ppt. 9	$(NH_4)_2S$	Black ppt.	Br, I, CNS dissolved	Ag_2S	NH_4Br, NH_4I, NH_4CNS
12.	Sol. 11	HNO_3, $Fe(NO_3)_3$	Red color	CNS pres.	X	$Fe(CNS)_3$, HBr, HI

TABLE 9—*Continued*

GROUP 1 ACID RADICALS

(*S*, $Fe[CN]_6^{IV}$, $Fe[CN]_6^{III}$, *Cl*, *CNS*, *Br*, *I*)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
13.	Sol. 12 (1 c.c.)	$HgCl_2$	Decolorization	CNS conf.	X	$Hg(CNS)_2$
14.	Sol. 12 (rest)	H_2O_2, CCl_4	Violet color (CS_2)	I pres.	X	I_2 in CS_2 HBr
15.	Sol. 14	$Cl_2(H_2O)$, CCl_4	Brown color (CS_2)	Br pres.	X	Br_2 in CS_2

PRECIPITATION AND ANALYSIS OF THE CHLORIDE GROUP (GROUP 1 ACID RADICALS)

Definition. — Those anions whose silver salts are insoluble in dilute solutions of nitric acid.

(38) **Detection and Removal of Sulphides.** — To 1 or 2 c.c. of the prepared solution from (**36 a, b,** or **c**) add 3 c.c. of H_2O and 1 drop of $Pb(NO_3)_2$ solution ①. A grayish black or black precipitate indicates the presence of **Sulphides.** A white precipitate ② indicates that sulphides are absent.

If sulphides are present, they should be removed as follows: carefully acidify a 12 c.c. sample of the solution from (**36a, b,** or **c**) with $HC_2H_3O_2$ and boil ③ *gently* until a piece of filter paper wet with $Pb(C_2H_3O_2)_2$ is no longer blackened when held in the vapor of the boiling solution. Filter from any precipitate ④, discard the precipitate, and treat the filtrate by (**39**).

If sulphides were absent, 8 c.c. of the same solution (**36a, b,** or **c**) above should be treated in the same way to remove carbonates and the filtrate treated by (**39**).

(39) **Detection of the Cyanogen Group.** — To 2 c.c. of the filtrate from (**38**) add 2 c.c. of $Ni(NO_3)_2$ and let the mixture stand for ten minutes or more, shaking vigorously at intervals. A precipitate ⑤ or decided turbidity ⑥ indicates the presence of **Ferrocyanide** or **Ferricyanide.** Discard the precipitate and filtrate. If no precipitate forms, (**40**) and (**41**) may be omitted. Treat the remainder of the filtrate from (**38**) by (**42**).

(40) **Separation and Detection of Ferrocyanides** ⑦. — To the remainder of the filtrate from (38) add 3 c.c. of HNO_3, and $(NH_4)_2MoO_4$* until precipitation is complete. (A slight excess of the reagent should be added since the precipitate is somewhat soluble in $K_4Fe[CN]_6$. In addition the same reagent is used in the test for ferricyanides, and the slight excess gives a desirable indication of their presence, as will be seen.) A mahogany-red precipitate ⑧ indicates the presence of **Ferrocyanides** and is $Na_2(MoO_2.Fe[CN]_6)_3.2MoO_3.20H_2O$. Filter, discard the precipitate, and treat the filtrate by (41).

(41) **Separation and Detection of Ferricyanides.** — Add NH_4OH to the filtrate from (40) until the solution is just alkaline, then add Na_2SO_3 ⑨, 1 c.c. at a time until any yellow color disappears (unless chromates are present). If there was no yellow color ⑩ apparent originally, 1 c.c. of Na_2SO_3 is sufficient, and in any case not more than 4 c.c. is needed. Acidify this solution carefully with HNO_3 ⑪ and note whether any red precipitate is formed when the mixture is gently warmed. If such is the case, add $(NH_4)_2MoO_4$ reagent until precipitation is complete. A mahogany-red precipitate indicates the presence of **Ferricyanides** and is $Na_2(MoO_2.Fe[CN]_6)_3.2MoO_3.20H_2O$. Filter, discard the precipitate, and treat the filtrate by (42).

(42) **Precipitation of Thiocyanates and Halides.** — To the filtrate from (41) (or [38] + 1 c.c. HNO_3) add $AgNO_3$ until precipitation ⑫ is complete. The end of the precipitation is indicated by the fact that the precipitate settles readily on warming and leaves a clear or only slightly turbid ⑬ liquid above. A yellow or white precipitate indicates the presence

* A specially prepared solution of $(NH_4)_2MoO_4$ should be used in this test because that prepared in the usual way is so strong in HNO_3 that it may decompose the ferricyanides and thiocyanate somewhat. The solution for this procedure may be prepared as directed on p. 212.

of thiocyanates, chlorides, iodides, and bromides. (If the precipitate is pure white, the latter two are probably absent ⑭). Filter and wash the precipitate with H_2O containing a few drops of HNO_3. Discard the filtrate and treat the precipitate by (**43**).

(**43**) **Separation and Detection of Chloride.** — Transfer the precipitate from (**39**), which may consist of AgCl, AgBr, AgI, AgCNS, to a test-tube or small flask, add 15 c.c. of "chloride-reagent" ⑮ (0.25*N* NH_4OH, 0.01N $AgNO_3$, and 0.25N KNO_3) and shake vigorously for three minutes. Filter, wash the precipitate with hot H_2O, and treat by (**44**). Acidify the filtrate with a minimum quantity of HNO_3. A white precipitate ⑮ which coagulates into flocks on warming and turns lavender on standing in the light indicates the presence of **Chloride.** A very faint opalescent precipitate which will not coagulate on warming and standing, should not be reported as chloride ⑯.

(**44**) **Solution of Thiocyanates, Iodides, and Bromides.** — Transfer the precipitate which was not dissolved by the "chloride reagent," and which may consist of AgCl (from incomplete solution by the chloride reagent), AgCNS, AgI, and AgBr, and treat it with 5 c.c. of concentrated NH_4OH ⑰. To this add $(NH_4)_2S$, drop by drop, with shaking and warming until further addition of the reagent no longer causes any precipitation ⑱. The precipitate should be stirred and tamped with a glass rod to disintegrate ⑲ it so that any unconverted silver halides covered with Ag_2S, will be exposed to the action of the reagent. (This is very important!) Boil the mixture for two or three minutes and filter, discarding the precipitate. Boil the filtrate until it no longer smells of ammonia. If the volume has become very small, add 3 c.c. of H_2O. Filter if there is any precipitate ⑳. Treat the solution or filtrate by (**45**).

(45) **Detection of Thiocyanates.** — To the filtrate from (44) add 1 c.c. of HNO_3 and *1 drop* of $Fe(NO_3)_3$. A deep red coloration indicates the presence of **Thiocyanates** and is due to the formation of weakly ionized $Fe(CNS)_3$ (21). (A brown color, due to oxidation of iodides by Fe^{+++}, may result if the amount of iodides is large or too much $Fe(NO_3)_3$ is added.) If the red color is doubtful add some $HgCl_2$ to 1 c.c. of the solution. The red color will disappear (22) if it is due to thiocyanates. Treat the remainder of the red solution by (46).

(46) **Detection of Iodides.** — To the solution from (42), which may contain thiocyanates, bromides, and iodides, add 2 c.c. of CCl_4 and 3 c.c. of H_2O_2 (23). Shake vigorously for a minute and let the CCl_4 settle to the bottom. A rich violet or purple solution of free I_2 dissolved in CCl_4 (24) indicates the presence of **Iodides.** If the color does not appear add 1–2 c.c. more of H_2O_2 (25) and shake vigorously again before reporting iodides absent. Filter the solution to remove the CCl_4 layer and boil it vigorously for three minutes, to remove iodine (26) and excess H_2O_2. Repeat the test with CCl_4 and H_2O_2 on 2 c.c. of this boiled solution to see if all iodine has been removed. If not, add 2 c.c. of H_2O to the main bulk of the boiled solution (which has meanwhile been cooled), shake vigorously, and boil again. Treat the solution, after all iodine and excess H_2O_2 have been removed, by (47) for the detection of bromides.

(47) **Detection of Bromides.** — To the solution from (43), from which all iodides have been removed, add 2 c.c. of CCl_4 and 3–5 c.c. of chlorine water (27). Shake the solution vigorously for a minute or more and allow the CCl_4 to settle. An amber brown or a yellow color in the CCl_4 layer indicates the presence of **Bromides** and is due to free Br_2 dissolved in CCl_4. Discard the whole mixture.

NOTES ON THE PRECIPITATION AND ANALYSIS OF THE CHLORIDE GROUP: GROUP 1 ACID RADICALS

1. The test for sulphides is made in the alkaline Na_2CO_3 solution for the reasons that, in the effervescence resulting from CO_2 when the solution is acidified, much H_2S might also be lost; in addition, oxidizing agents, such as sulphides or nitrites, which do not affect sulphides readily in alkaline solution, would immediately oxidize it in acid solution.

If the test for sulphides at this point is negative, they should not be reported absent until procedure (**60**) has been carried out, because many of the sulphides of the metals are affected but little by boiling with Na_2CO_3.

* * *

2. The black precipitate is due to PbS. A white precipitate is due to the formation of $PbCO_3$, and although the concentration of the $CO_3^=$ ion is usually much higher than that of the $S^=$ ion, the precipitation of sulphides will be practically complete as was pointed out in Note **3**, p. 147.

* * *

3. H_2S is the only acid of this group which is appreciably volatile and may thus be removed by boiling. The others are practically not affected by this treatment.

* * *

4. The precipitate which may result at this point is due to certain amphoteric compounds, such as SnO_2, SiO_2, and free S, which are soluble in the alkaline solution of the Na_2CO_3 but insoluble in weakly acid solution.

* * *

5. Ferrocyanides and ferricyanides form insoluble Ni salts in acetic acid solution, of the compositions $Ni_2Fe(CN)_6$ and $Ni_3(Fe[CN]_6)$ respectively. The ferrocyanide is greenish white, the ferricyanide is yellowish green. They are quite insoluble, being unaffected by dilute HCl.

6. A turbidity and not a distinct precipitate may result from the fact that the ferrocyanide and ferricyanide of Ni tend to enter the colloidal form very readily and consequently do not coagulate well.

* * *

7. Ferrocyanides and ferricyanides are extremely weakly ionized complex ions resulting respectively from the solution of $Fe(CN)_2$ and $Fe(CN)_3$ by excess KCN. They derive their names from the fact that the ferrocyanide contains ferrous iron and the other ferric iron, despite the fact that the former complex is tetravalent and the latter only trivalent:

$FeCl_2 + 2KCN \rightarrow 2KCl + Fe(CN)_2$.
$Fe(CN)_2 + 4KCN \rightarrow K_4Fe(CN)_6$.
$FeCl_3 + 3KCN \rightarrow 3KCl + Fe(CN)_3$.
$Fe(CN)_3 + 3KCl \rightarrow K_3Fe(CN)_6$. (See *Theory*, p. 145, etc.)

* * *

8. The separation of ferrocyanides from ferricyanides depends on the fact that in acid solution the latter do not give any precipitate with $(NH_4)_2MoO_4$. This test is delicate enough for 1 mg. of ferrocyanides to be detected in the presence of 200 mg. of ferricyanides.

* * *

9. Ferricyanides in alkaline solutions are strong oxidizing agents and are therefore readily reduced by a Na_2SO_3 solution to ferrocyanides:

$$2Na_3Fe(CN)_6 + Na_2SO_3 + 2NH_4OH \rightarrow 2Na_4Fe(CN)_6 + (NH_4)_2SO_4 + H_2O.$$

* * *

10. As little as 1 mg. per c.c. of ferricyanides imparts a detectable yellow color to the solution. An equal amount of ferrocyanides does not give a detectable yellow. In any event 4 c.c. of a normal solution of

freshly prepared Na_2SO_3 is equivalent to about 800 mgs. of ferricyanide and is therefore more than enough to remove the maximum amount of the latter which may be expected under ordinary conditions.

* * *

11. $Na_2(MoO_2.Fe[CN]_6)_3.2MoO_3$ is soluble in alkaline solution and insoluble in fairly strong acid solution.

* * *

12. See Note **4**, p. 148.

* * *

13. The turbidity at this point may be due to the fact that the amorphous silver halides tend to remain suspended but are usually coagulated on warming.

* * *

14. See Note **5**, p. 148.

* * *

15. AgCl will dissolve in NH_4OH by virtue of the formation of the weakly ionized complex ion $Ag(NH_3)^+_2$ (see *Theory*, p. 143). The other Ag salts of this group, being more insoluble than AgCl, show less tendency to dissolve in NH_4OH. This is especially so in the presence of $AgNO_3$, the Ag^+ ion of which tends to lessen the solvent power of the NH_3 by uniting with it. The solubility of AgCl in NH_4OH-$AgNO_3$ mixtures has been carefully studied and it is possible to prepare a solution of the two of such strength that it will dissolve sufficient AgCl to give a satisfactory test and yet dissolve only the faintest traces of the other insoluble silver salts of these four. Thus, a solution which is $0.25N$ in NH_4OH and $0.01N$ in $AgNO_3$ dissolves so little AgCNS (the next in order of solubility) as to give only the faintest haze when acidified with HNO_3. The KNO_3 is added to prevent formation of colloidal solutions.

16. As stated in the previous note, a very faint opalescence may be due to the solution of small amounts of AgCNS by the "chloride reagent," and their reprecipitation by acidification of the solution.

* * *

17. Concentrated NH_4OH is added because it will dissolve AgBr completely and AgI somewhat. This again is due to the formation of the complex $Ag(NH_3)_2^+$ (see *Theory*, p. 143). The conversion of AgBr and AgI to Ag_2S is assisted by having them in solution rather than in the solid form.

* * *

18. The conversion of AgBr and AgI (even from the solid form) depends upon the extremely low solubility of Ag_2S. The same reasoning applies here as was used in Note **3**, p. 147.

* * *

19. When AgI is treated with concentrated NH_4OH, that part of it which does not go into solution forms a gummy mass. Ag_2S precipitates upon the surface of this, and unless it is disintegrated the conversion of AgI will not be complete. Too much care cannot be exercised at this point. Loss of iodides and bromides by incomplete conversion at this point is the commonest source of error in this group.

* * *

20. On boiling the solution, $(NH_4)_2S$ is decomposed to H_2S and NH_3, and the former is oxidized in part to free S by oxygen of the air. Hence the possible formation of a precipitate.

* * *

21. The red coloration of $Fe(CNS)_3$ is due to the fact that this compound is rather weakly dissociated. This must be so since neither the Fe^{+++} ion nor the CNS^- ion is red.

* * *

22. The red color of $Fe(CNS)_3$ is removed because of the formation of the even more weakly ionized $Hg(CNS)_2$, which is colorless.

23. The test for iodides depends on the fact they are oxidized to free I_2 by H_2O_2,

$$2KI + 2HNO_3 + H_2O_2 \rightarrow 2KNO_3 + 2H_2O + I_2$$

whereas bromides are not.

* * *

24. The use of CCl_4 depends on the partition law, that a substance soluble in two immiscible solvents distributes itself between the two in proportion to its solubility in each, at a given temperature. The ratio of the distribution between the two solvents is independent of the quantity of the two solvents used. For CCl_4 and H_2O at 25°, this ratio is 85 to 1, which means the concentration of I_2 will be 85 times as great in the CCl_4 layer as in the H_2O layer. The distribution ratio at the same temperature for Br_2 is only 23:1.

* * *

25. Thiocyanates are oxidized rather easily to sulphates, so that if they are present in large quantity, H_2O_2 will be consumed in oxidizing them. For this reason a second addition of H_2O_2 is recommended.

* * *

26. The solution is boiled to remove I_2 since it is thus more readily and quickly removed than by extraction with CCl_4. It is necessary to remove it because it would conceal the less distinct yellow color of Br_2 in the CCl_4 layer.

CCl_4 will not run through ordinary filter paper and may thus be separated from the aqueous solution by filtration.

* * *

27. The liberation of Br_2 depends upon the fact that it is displaced from its compounds by the more active Cl_2:

$$2HBr + Cl_2 \rightarrow 2HCl + Br_2.$$

SUMMARY OF GROUP 1 ACID RADICALS

The principles of separation applied in this group are:

1. (Of the heavy metals) that their hydroxides and carbonates (with a few exceptions) are insoluble.

2. (Of the group) that their silver salts are insoluble in strong acid solution.

3. (Of ferrocyanides from the remaining radicals) that the complex compound with $(NH_4)_2MoO_4$ is insoluble in strong acid solution.

4. (Of ferricyanides from the remaining radicals) that ferricyanides are quickly and completely reduced to ferrocyanides in alkaline solution, and may then be precipitated in acid solution as above.

5. (Of chlorides from the remaining radicals) that AgCl, only, is soluble in a solution of NH_4OH whose OH ion concentration is controlled by dilution, and use of $AgNO_3$.

6. (Of thiocyanates from the remaining radicals [not a separation]) that $Fe(CNS)_3$ has a deep red color.

7. (Of iodides from bromides) that iodides are readily oxidized in acid solution by H_2O_2.

Equations on Group 1 Acid Radicals

Note: The student should look up, in the tables on pp. 222 *et seq.* in the Appendix, the products of the reactions of the metallic nitrates (except in the cases of arsenic, antimony, and tin, in which chlorides are used) when boiled with sodium carbonate, in preparation of the solution.

REDUCING AGENTS

1. Potassium ferricyanide and sodium sulphide.
2. Potassium ferricyanide and sodium iodide.
3. Potassium ferricyanide, sodium sulphite, and water.
4. Potassium ferricyanide, sodium nitrite, and water.
5. Potassium ferrocyanide and ferric chloride.

SULPHIDES

1. Sodium sulphide and silver nitrate.
2. Sodium sulphide and lead nitrate.
3. Sodium sulphide and acetic acid (boiled).

FERROCYANIDES

1. Sodium ferrocyanide and silver nitrate.
2. Sodium ferrocyanide and ammonium molybdate (no reaction need be written in this case, since it is too complex for elementary work).

FERRICYANIDES

1. Sodium ferricyanide and ammonium molybdate.
2. Sodium ferricyanide, ammonium hydroxide, and sodium sulphite.
3. Sodium ferrocyanide and ammonium molybdate (see eq. 2 under FERROCYANIDES).

CHLORIDES

1. Sodium chloride and silver nitrate.
2. Sodium chloride and ammonium molybdate.
3. Sodium chloride and sodium sulphite.
4. Sodium chloride and silver nitrate.
5. Silver chloride and ammonium hydroxide (in the presence of silver and potassium nitrates).
6. Silver ammonia chloride and nitric acid.

THIOCYANATES

1. Sodium thiocyanate and silver nitrate.
2. Sodium thiocyanate and ammonium molybdate.
3. Sodium thiocyanate and sodium sulphite.
4. Sodium thiocyanate and silver nitrate.
5. Silver thiocyanate and ammonium hydroxide (in presence of silver and potassium nitrates).
6. Silver thiocyanate and ammonium sulphide.
7. Ammonium thiocyanate and ferric nitrate.
8. Ferric thiocyanate and mercuric chloride.

IODIDES

1. Sodium iodide and silver nitrate.
2. Sodium iodide and ammonium molybdate.
3. Sodium iodide and sodium sulphite.
4. Sodium iodide and silver nitrate.
5. Silver iodide and ammonium hydroxide (in the presence of silver and potassium nitrates).
6. Silver iodide and ammonium sulphide.
7. Ammonium iodide and ferric nitrate.
8. Ammonium iodide, nitric acid, and hydrogen peroxide.
9. Iodine and carbon tetrachloride (no reaction).

BROMIDES

1. Sodium bromide and silver nitrate.
2. Sodium bromide and ammonium molybdate.
3. Sodium bromide and sodium sulphite.
4. Sodium bromide and silver nitrate.
5. Silver bromide and ammonium hydroxide (in the presence of silver and potassium nitrates).
6. Silver bromide and ammonium sulphide.
7. Ammonium bromide and ferric nitrate.
8. Ammonium bromide, nitric acid, and hydrogen peroxide.
9. Ammonium bromide and chlorine (water).
10. Bromine and carbon tetrachloride (no reaction).

Questions on Group 1 Acid Radicals

(See also *Theory*, pp. 168–173.)

1. What is the basis of the separation for ferrocyanides from ferricyanides?
2. Why is the solution in which ferricyanides are reduced made alkaline before addition of Na_2SO_3?
3. What is the basis of the separation of chlorides from thiocyanates, bromides, and iodides?
4. What is the purpose of the $AgNO_3$ in the "chloride" reagent? of the KNO_3?

5. Which of the remaining four Ag salts would be most likely to dissolve in the "chloride" reagent? Upon what fact does your answer depend?
6. What is the faint turbidity which sometimes results from the acidification of the "chloride" reagent after filtration, even when chlorides are absent? Does this substantiate your answer to the previous question?
7. Explain the conversion of the insoluble silver salts of the thiocyanates, bromides, and iodides to soluble ammonium salts by $(NH_4)_2S$.
8. Why is only one drop of $Fe(NO_3)_3$ added in the test for thiocyanates?
9. What proof have we that $Fe(CNS)_3$ is not completely dissociated?
10. Explain the confirmatory test for thiocyanates.
11. Why, if the red color were doubtful, would it be advisable to confirm thiocyanates? What else might be formed that could be misleading at this point?
12. What is the basis for distinguishing between iodides and bromides?
13. Of what law do we take advantage to make the liberation of iodine visible?
14. Can this law be applied with as much advantage in the test for bromides?
15. What is the basis for the separation of Group 1 acids from the other groups?

TABLE 10

Group 2 Acid Radicals

(SO_4, SO_3, CrO_4, C_2O_4, F)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Sol. 1 (Table 9)	$HC_2H_3O_2$, $BaCl_2$, $CaCl_2$	Colored ppt.	Group 2 acids pres.	$BaSO_4$, $BaSO_3$, $BaCrO_4$, CaC_2O_4, CaF_2	X
2.	Sol. 1 (Table 9)	HNO_3, $AgNO_3$	Colored ppt.	S and CNS removed	Ag_2S and AgCNS, etc.	Na_2SO_4, Na_2SO_3, Na_2CrO_4, NaF, $Na_2C_2O_4$, etc.
3.	Sol. 2	HCl	Wh. pt.	Ag rem'd.	AgCl	Na_2SO_4, Na_2SO_3, Na_2CrO_4, NaF, $Na_2C_2O_4$, etc.
4.	Sol. 3	$BaCl_2$	White ppt.	SO_4 pres.	$BaSO_4$	Na_2SO_3, Na_2CrO_4, NaF, $Na_2C_2O_4$
5.	Sol. 4	$Br_2(H_2O)$	White ppt.	SO_3 pres.	$BaSO_4$	Na_2CrO_4, NaF, $Na_2C_2O_4$

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
6.	Sol. 5	$NH_4C_2H_3O_2$, $CaCl_2$	Colored ppt.	CrO_4, C_2O_4, and F pres.	$BaCrO_4$, CaF_2, CaC_2O_4	X
7.	Ppt. 6 (half)	HNO_3, MnO_2, $Ba(OH)_2$	White ppt.	C_2O_4 pres.	$BaCO_3$	X
8.	Ppt. 6 (rest)	H_2SO_4, SiO_2, H_2O	Turbidity	F pres.	H_2SiO_3	X

PRECIPITATION AND ANALYSIS OF THE SULPHATE GROUP: GROUP 2 ACID RADICALS

[SO_4, SO_3, CrO_4, C_2O_4, F]

Definition. — Those anions whose barium or calcium salts are insoluble in weakly acid solutions in the presence of ammonium salts.

(48) Precipitation and Detection of Sulphate. — If the Group 2 acid radicals were shown to be present in (**37b**) and either CNS^- or $S^=$ ① or both were found in Group 1, *carefully* make 10 c.c. of the solution from (**36a, b,** or **c**) very slightly acid with HNO_3, and add $AgNO_3$ until precipitation is complete. Filter, discard the precipitate, and treat the filtrate in the same manner as directed in the next paragraph for a solution which did not contain thiocyanates or sulphides, first removing the excess Ag by adding HCl until precipitation is complete.

Carefully acidify a 10 c.c. sample from (**36a, b,** or **c**) and which does not contain any sulphides or thiocyanates with HNO_3, taking care to have only a very slight excess. To this solution (filtered from any precipitate if necessary), or the filtrate from the paragraph above, add a 1 c.c. excess of HNO_3 and 4–5 c.c. of $BaCl_2$. A white precipitate which should be allowed to stand for a few minutes indicates the presence of **Sulphates** and is $BaSO_4$ ②. Filter, reject the precipitate, and treat the filtrate by (**49**) for sulphites.

(49) Detection of Sulphites. — To the filtrate from (**48**), which may contain $BaSO_3$, BaC_2O_4, $BaCrO_4$, and BaF_2, add saturated Br_2 water drop by drop until after the gas has been blown away from the surface, the liquid still smells of Br_2.

Heat the mixture just to boiling. A white precipitate indicates the presence of **Sulphites** and is $BaSO_4$ ③. Filter, reject the precipitate, and treat the filtrate by (**50**) for the detection of chromates, oxalates, and fluorides.

(**50**) **Precipitation and Detection of Chromates, Oxalates, and Fluorides.** — Evaporate the filtrate from (**49**) to a volume of 10 c.c. Add 2 c.c. of a 50 per cent solution of $NH_4C_2H_3O_2$ and 5 c.c. of 6*N* $CaCl_2$ ④. Warm the mixture gently for a few minutes and allow it to stand for ten minutes longer. A yellow precipitate (which is best sought on the filter) indicates the presence of **Chromates** and is $BaCrO_4$ ⑤. If the precipitate is pure white, chromates are absent and the presence of **Oxalates** and **Fluorides** is indicated. In any event, if a precipitate forms, it should be tested for oxalates and fluorides. To do this, divide the precipitate equally by filtering on two filters, wash thoroughly, and discard the filtrate.

(**51**) **Confirmatory Test for Fluorides** ⑥. — Treat one of the two parts of the precipitate from (**50**) as follows: Tear away the portions of the filter paper on which there is no precipitate and dry the remainder over a small free flame or water bath. If the precipitate is very small, it is best to incinerate the paper and precipitate in a spiral of platinum wire. Remove the precipitate from the paper and mix it, or the ash if the incineration was carried out, with about twice its quantity of finely ground *natural* ⑦ quartz. Transfer the mixture to a small thoroughly dried test-tube and add H_2SO_4 (95 per cent) drop by drop (use a dropper) to make a thin paste. Care should be taken not to wet the sides of the tube with H_2SO_4. Insert a narrow piece of glass tubing in a small cork which will fit the test-tube. Dry this glass tube on the outside and moisten it on the inside. Insert the glass tube in the test-tube so that the bottom of the

glass tube is about an inch from the mixture in the test-tube. (See Figure 6.) Fix it there by means of the cork, and heat the mixture gently over a small free flame for a minute or two. A white precipitate on the wet portion of the tube indicates the presence of **Fluorides** and is H_2SiO_3 ⑧.

(52) Confirmatory Test for Oxalates. — Pour 5 c.c. of hot HNO_3 repeatedly over the filter containing the other half of the precipitate from (**50**). To this solution in a test-tube add $\frac{1}{2}$ g. of powdered MnO_2 which has been previously boiled for a minute or more with dilute HNO_3, and fit the test-tube with a safety tube and delivery-tube the end of which is submerged in a solution of $Ba(OH)_2$ in another test-tube, as shown in Figure 7. Boil the HNO_3-MnO_2 mixture gently for several minutes while allowing the escaping gases to pass through the $Ba(OH)_2$ solution. A white precipitate forming in the $Ba(OH)_2$ solution indicates the presence of **Oxalates** and is $BaCO_3$. A blank test ⑩ should always be made, using the same reagents and methods but omitting the precipitate of CaC_2O_4 (or CaF_2 or both). The precipitate obtained in the regular procedure should then be compared with any obtained in the blank test.

NOTES ON THE PRECIPITATION AND DETECTION OF THE SULPHATE GROUP

1. The sulphides and thiocyanates are removed to prevent interference with the sulphite test when Br_2 is added. The latter would oxidize sulphides to free sulphur and thiocyanates to sulphates, giving a precipitate which might be mistaken for $BaSO_4$:

$$Br_2 + HOH \rightarrow HBrO + HBr.$$
$$H_2S + HBrO \rightarrow HBr + H_2O + S.$$
$$13Br_2 + 14H_2O + 2NaCNS + 2HNO_3 \rightarrow 2NaNO_3 + 26HBr + 2CO_2 + 2NO + 2H_2SO_4.$$

FIGURE 6
The Fluoride Test

FIGURE 8
The Borate Test

FIGURE 7
Apparatus for Oxalate, Carbonate and Sulphide Tests
(Test-tubes may be substituted for flasks)

2. $BaSO_4$, a salt of a strong acid, can be precipitated in HNO_3 solution, whereas the Ba salts of the other weaker acids of this group are not precipitated under these conditions. (See *Theory*, pp. 120–21.)

* * *

3. H_2SO_3 is oxidized by Br_2 to H_2SO_4, from which $BaSO_4$ is precipitated to give the test for sulphites:

$$Br_2 + HOH \rightarrow HBrO + HBr.$$
$$H_2SO_3 + HBrO \rightarrow H_2SO_4 + HBr.$$

* * *

4. $CaCl_2$ is added at this point because the Ba salts of oxalate and fluoride are too soluble to be precipitated unless present in moderate quantity. The corresponding Ca salts will precipitate with less than 1 mg. of oxalate or fluoride present.

* * *

5. $NH_4C_2H_3O_2$ is added to reduce the acidity of the solution by formation of the weakly ionized acetic acid (see *Theory*, p. 116). This is necessary because $BaCrO_4$, CaC_2O_4, and CaF_2, being salts of relatively weak acids, would be soluble in HNO_3 solution.

* * *

6. The test for fluorides must be very carefully carried out, particularly with regard to keeping the apparatus dry and using 95 per cent H_2SO_4, because the test depends on the formation of SiF_4 which might be hydrolyzed by any H_2O present, before it reached the inside of the moist tube:

$$SiF_4 + 4HOH \rightarrow H_4SiO_4 + 4HF.$$

* * *

7. Natural quartz and not artificial SiO_2 should be used in the test for fluorides. The latter tends to form $SiOF_2$ and thus diminishes the sensitivity of the test.

8. The test for fluorides depends upon the formation first of HF from CaF_2 and H_2SO_4; this in turn reacts with SiO_2 to form SiF_4, which is hydrolyzed by the water in the moist tube to form a gelatinous turbidity of H_4SiO_4.

$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF.$
$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$ (removed by conc. H_2SO_4).
$SiF_4 + 4HOH \rightarrow H_4SiO_4 + 4HF.$

* * *

9. The confirmatory test for oxalates depends upon the oxidation of oxalic acid by MnO_2, forming CO_2, which on passing into $Ba(OH)_2$ precipitates $BaCO_3$:

$CaC_2O_4 + 2HNO_3 \rightarrow H_2C_2O_4 + Ca(NO_3)_2.$
$H_2C_2O_4 + MnO_2 + 2HNO_3 \rightarrow Mn(NO_3)_2 + 2H_2O + 2CO_2.$
$2Ba(OH)_2 + CO_2 \rightarrow 2BaCO_3 + 2H_2O.$

CaC_2O_4 is soluble in HNO_3 because of the formation of the more weakly ionized $H_2C_2O_4$. (See *Theory*, p. 120).

* * *

10. The blank test is advisable because of the possible presence of dirt or organic material which might be oxidized to CO_2 and thus give a precipitate of $BaCO_3$. For this reason the MnO_2 is first boiled separately with HNO_3 to oxidize any extraneous material.

SUMMARY OF GROUP 2 ACID RADICALS

The principles of separation applied in this group are:

1. (Of the group) that the Ba and Ca salts are insoluble in weakly acid solutions in the presence of ammonium salts.

2. (Of SO_4 from the remaining radicals) that $BaSO_4$ is insoluble in solutions of strong acids.

3. (Of SO_3 from the remaining radicals) that SO_3 is oxidized to SO_4 by Br_2 water.

4. (Of separation of CrO_4 from the remaining radicals — no separation) detected by the fact that $BaCrO_4$ is yellow.

5. (Of C_2O_4 from F) that C_2O_4 is oxidized to CO_2 by MnO_2 and HNO_3.

Equations on Group 2 Acid Radicals

SULPHATES

1. Sodium sulphate and calcium chloride.
2. Sodium sulphate and barium chloride.

SULPHITES

1. Sodium sulphite and calcium chloride.
2. Sodium sulphite and barium chloride (in weak acid solution and strong acid solution).
3. Sodium sulphite and bromine water (two reactions).
4. Sodium sulphate and barium chloride.

CHROMATES

1. Sodium chromate and calcium chloride.
2. Sodium chromate and barium chloride (in weak acid solution and in strong acid solution).
3. Barium chromate and nitric acid.

FLUORIDES

1. Sodium fluoride and calcium chloride.
2. Sodium fluoride and barium chloride.
3. Calcium fluoride and nitric acid.
4. Calcium fluoride, sulphuric acid (conc.), and silica.
5. Silicon tetrafluoride and water.

OXALATES

1. Sodium oxalate and calcium chloride.
2. Sodium oxalate and barium chloride.
3. Calcium oxalate and nitric acid.
4. Oxalic acid, nitric acid, and manganese dioxide.
5. Carbon dioxide and barium hydroxide.

Questions on Group 2 Acid Radicals

(See also *Theory*, pp. 168–173.)

1. Under what conditions could all of the radicals of this group be precipitated simultaneously?
2. Which Ba salts of the Group 2 acids are insoluble in strong acids? Is this fact taken advantage of in the separations of the group?
3. Account for the fact that the same reagent may be used to test both for sulphates and for sulphites.
4. What are the similarities and differences between the confirmatory test for oxalates and the test for carbonates?
5. Why is it always advisable to make a blank test with the reagents along with the oxalate test?
6. Why must the apparatus in the test for fluorides be scrupulously dry?
7. Suggest another test for fluorides. Summarize the objections to both of these tests for fluorides.

TABLE 11

Group 3 Acid Radicals

(NO_2, NO_3, BO_2, AsO_3, AsO_4)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
1.	Sol. 1 (Table 9)	NaOH, Al, Litmus	Litmus red → blue	NO_2 and NO_3 pres.	X	(NH_4OH)
2.	Sol. 1 (Table 9)	HCl, KI, starch paper	Blue color	NO_2 pres.	(I_2)	X
3.	Sol. 1 (Table 9)	H_2SO_4, $FeSO_4$	Brown ring	NO_3 pres.	($FeSO_4.2NO$)	X
4.	Sol. 1 (Table 9)	$HC_2H_3O_2$, Turmeric	Red-brown color	BO_2 pres.	X	X
5.	Sol. 1 (Table 9)	HNO_3, H_2S	Yellow ppt.	AsO_3 pres.	As_2S_3	X

TABLE 11—*Continued*

GROUP 3 ACID RADICALS

(*NO_2, NO_3, BO_2, AsO_3, AsO_4*)

No.	*Substance*	*Reagent*	*Result*	*Inference*	*Precipitate*	*Solution*
6.	Sol. 1 (Table 9)	HNO_3, NH_4OH, Magnesia mixture	White ppt.	AsO_4 prob. pres.	$MgNH_4PO_4$	X
7.	Ppt. 6	$HC_2H_3O_2$, $AgNO_3$	Red ppt.	AsO_4, confirmed	Ag_3AsO_4	X

DETECTION OF THE REMAINING (UNCLASSIFIED) ACID RADICALS (GROUP 3 ACID RADICALS)

[NO_2, NO_3, BO_3, AsO_4, AsO_3]

Definitions. — Those anions which have no common precipitating agent.

(53) Preliminary Test for Nitrites and Nitrates. — To 3 c.c. of the Na_2CO_3 solution from (**36a, b,** or **c**) add 3 c.c. of NaOH, and boil gently for two to three minutes to insure removal of all NH_3. Place the solution in a small beaker and add 1 g. of aluminum ① turnings or a small piece of granulated zinc ① and some iron filings. Cover the beaker with a dry watch glass on the bottom of which is pasted a piece of moist red litmus paper. Warm the mixture on the water bath for several minutes. If the paper turns blue (because of formation of NH_3), the presence of nitrites or nitrates or both ② is indicated. If the paper does not turn blue the tests for nitrites and nitrates, (**54**) and (**55**), may be omitted.

(54) Detection of Nitrites ③. — Acidify 3 c.c. of the Na_2CO_3 solution from (**36a, b,** or **c**) with HCl, using the small test-tube from the fluoride test. Shake but do not warm ④ to remove CO_2. Paste a piece of wet KI-starch paper around the end of the glass rod used in the fluoride test and insert the rod into the test-tube (see Figure 6) so that the paper is about two inches from the surface of the liquid; hold the rod in place by means of the cork. Warm the solution very gently for a few minutes. *Do not boil* ⑤.

A blue color ⑥ on the KI-starch paper indicates the presence of **Nitrites** and is due to the liberation of free I_2 ⑦.

(55) Detection of Nitrates. — If the constituents mentioned in Note **8** below are known to be absent, acidify 3 c.c. of the Na_2CO_3 solution from (**36a, b**, or **c**) with H_2SO_4 and warm to remove CO_2. Cool this solution thoroughly under the tap and add 3–5 c.c. of concentrated H_2SO_4, a little at a time. Cool ⑨ after each addition. Hold a test-tube containing 5 c.c. of a solution of freshly prepared ⑩ $FeSO_4$ in as nearly a horizontal position as possible, and pour the thoroughly cooled H_2SO_4 solution slowly and carefully down the side of the $FeSO_4$ test-tube. Care should be taken to prevent mixing ⑪ of the two solutions as far as possible, allowing the heavier H_2SO_4 solution to run underneath and support the lighter $FeSO_4$ solution. Let this mixture stand for at least fifteen minutes unless a brown ring forms sooner at the junction of the two liquids. This brown ring indicates the presence of **Nitrates** and is $FeSO_4.2NO$ ⑫.

(56) Detection of Borates. — Place 2–3 drops of an alcoholic solution of turmeric in an evaporating dish and add to it 2 c.c. of the Na_2CO_3 solution from (**36a, b,** or **c**). Acidify with $HC_2H_3O_2$ and evaporate to dryness on a water bath. A reddish brown residue indicates the presence of **Borates** ⑬.

Another test which may be used to advantage in the detection of borates depends on the formation of volatile methyl borate $(CH_3)_3BO_3$ ⑭, which burns with a green flame. Evaporate 3 c.c. of the Na_2CO_3 solution from (**36a, b,** or **c**) to dryness and transfer the residue to a small dry test-tube, such as was used in the fluoride test. Add 2 c.c. of conc. H_2SO_4 and 2 c.c. of methyl alcohol (ethyl alcohol may also be used). Draw a short piece of glass tubing to a tip in the flame (or use the nipple from a wash bottle), insert this into a cork and stopper the mouth of the small test-

tube with it. (See Figure 8.) Warm the mixture in the test-tube gently and ignite the issuing vapors at the tip of the glass nipple. If the vapors burn with a green flame the presence of borates is indicated.

(57) **Detection of Arsenite.** — If arsenic was found present in testing for the metals, take 3 c.c. of the Na_2CO_3 solution from (**36a, b,** or **c**), and just acidify it with HNO_3. Warm to remove any CO_2, dilute to 15 c.c. and pass in H_2S. A yellow precipitate, forming in a short time ⑮, indicates the presence of **Arsenites** and is As_2S_3 ⑯.

(58) **Detection of Arsenates.** — If arsenic was found present in testing for the metals, acidify 3 c.c. of the Na_2CO_3 solution from (**36a, b,** or **c**) with HNO_3, warm to remove CO_2 and make slightly alkaline with NH_4OH (if arsenites are present; otherwise add more NH_4OH ⑰). Filter from any precipitate, and add 5 c.c. of magnesia mixture (see arsenic test, p. 67). Warm the mixture and allow it to stand for ten minutes unless a precipitate forms sooner. A white precipitate indicates the presence of **Arsenate** (or phosphate if the latter was found present in the procedure for the metals). The precipitate may be $MgNH_4AsO_4$ ⑱ or $MgNH_4PO_4$. Filter and wash the precipitate with a minimum quantity of diluted NH_4OH. To 1 c.c. of $AgNO_3$ add a few drops of $HC_2H_3O_2$, and pour this mixture over the precipitate on the filter. A dark red precipitate confirms the presence of arsenates and is Ag_3AsO_4 ⑲. If the residue on the filter is yellow ⑳, dissolve as much of it as will dissolve in 3 c.c. of hot HCl by pouring the latter repeatedly over the precipitate on the filter. To the filtrate add $\frac{1}{2}$ c.c. of KI and 2 c.c. of CCl_4. Shake the mixture thoroughly and allow it to settle. A purple color in the CCl_4 layer confirms arsenates and is due to free I_2 dissolved in the CCl_4.

NOTES ON THE DETECTION OF GROUP 3 ACID RADICALS

1. Nitrites and nitrates are reduced by zinc or aluminum in alkali solution by the H_2 from the interaction of the metal and the alkali:

$$NaNO_3 + 4Zn + 7NaOH \rightarrow 4Na_2ZnO_2 + 2H_2O + NH_3.\uparrow$$

$$NaNO_2 + 3Zn + 5NaOH \rightarrow 3Na_2ZnO_2 + H_2O + NH_3.\uparrow$$

The NH_3 forms NH_4OH on the moist litmus as in the ammonium test.

* * *

2. Ferrocyanides, ferricyanides, and thiocyanates are also reduced to NH_3 under these conditions. If they are present, the Na_2CO_3 solution should be acidified with $HC_2H_3O_2$, shaken to remove any CO_2 (*warming would evolve NO_2!*), and treated with an excess of Ag_2SO_4. The insoluble Ag salts of the interfering acid radicals may then be filtered off and the solution made strongly alkaline with NaOH for the NO_2 and NO_3 test.

It is true that some of the nitrites may be lost when the solution is acidified with $HC_2H_3O_2$, but if the solution is not boiled, a sufficient quantity will remain to give a distinct test.

* * *

3. If the test given for nitrites leaves a doubtful result, an alternative test may be made by acidifying 2 c.c. of the Na_2CO_3 solution from (**36a, b,** or **c**) with $HC_2H_3O_2$ and distilling the oxide of nitrogen into 3 c.c. of NaOH using the apparatus for the oxalate test. Acidify this solution with dilute H_2SO_4, a little at a time, cooling between additions, to prevent loss of NO_2. To the acidified solution add 1 c.c. of freshly prepared $FeSO_4$ solution. A brown coloration indicates the presence of nitrites and is $FeSO_4.2NO$. The reactions are:

$NaNO_2 + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + HNO_2.$
$3HNO_2 \rightarrow H_2O + HNO_3 + 2NO.$
$2NO + O_2(air) \rightarrow 2NO_2.$
$2NO_2 + 2NaOH \rightarrow NaNO_3 + NaNO_2 + H_2O.$
$NaNO_2 + H_2SO_4 \rightarrow HNO_2 + NaHSO_4.$
$3HNO_2 \rightarrow H_2O + HNO_3 + 2NO.$
$FeSO_4 + 2NO \rightarrow FeSO_4.2NO.$

(See Note **12** — this section.)

* * *

4. The solution is not warmed or boiled to remove CO_2 because of the danger of boiling out the oxides of nitrogen from the decomposition of HNO_2. (See equation in previous note.)

* * *

5. The solution should not be boiled because of the danger of spattering some of the solution on the KI-starch paper. Should the solution contain other (non-volatile) oxidizing agents there is a possibility that I_2 might be liberated, through being spattered on to the paper.

* * *

6. Even though the solution is not boiled, the evolution of CO_2 or NO_2 may cause some spattering on the KI-starch paper, causing it to turn blue in spots. Unless the paper is uniformly blue (not speckled) the test should be looked upon with suspicion.

* * *

7. The reactions for the liberation of free I_2 from the KI are:

$$2KI + 4NO_2 + 2H_2O \rightarrow 2KNO_2 + 2NO + 2H_2O + I_2.$$

The formation of NO_2 from a nitrite was shown in Note **3** above.

The blue coloration is due to a reaction between the iodine and the starch, giving a deep blue color. The nature of the reaction is not exactly known.

8. Iodides, bromides, ferrocyanides, ferricyanides, chromates, and nitrites interfere with the test for nitrates and must first be removed. This is done as follows: Make the Na_2CO_3 solution from (**36a, b,** or **c**) as nearly neutral as possible with $HC_2H_3O_2$ but do not allow it to become acid. Boil the solution thoroughly with 5 c.c. of $(NH_4)_2SO_4$. This will remove nitrites:

$$2NaNO_2 + (NH_4)_2SO_4 \rightarrow Na_2SO_4 + 2NH_4NO_2.$$

$$NH_4NO_2 + (\text{heat}) \rightarrow N_2\uparrow + 2H_2O.$$

Acidify the boiled solution with H_2SO_4 and add Ag_2SO_4 in excess. Filter from the precipitate of $Ag_3Fe(CN)_6$, AgI, and AgBr. To the filtrate add Na_2SO_3 and allow the solution to stand for a few minutes. Finally, boil the solution to remove excess SO_2 and make alkaline with NH_4OH to precipitate $Cr(OH)_3$. Filter and test the filtrate for nitrates.

The chromates are reduced to trivalent chromium by H_2SO_3:

$$2K_2CrO_4 + 2H_2SO_4 + 3H_2SO_3 \rightarrow 2K_2SO_4 + Cr_2(SO_4)_3 + 5H_2O.$$

The iodides and bromides interfere because they are oxidized by conc. H_2SO_4 to liberate free Br_2 and I_2, which give the solution a brown color that looks like the nitrate ring:

$$2KI(Br) + 2H_2SO_4 \rightarrow K_2SO_4 + 2H_2O + SO_2 + I_2(Br_2).$$

The ferrocyanides and ferricyanides interfere because they are partially decomposed by concentrated H_2SO_4 to ferrous and ferric salts respectively. These with the undecomposed ferrocyanides and ferricyanides give the deep blue precipitates (Prussian and Turnbull's blue) which would obscure the nitrate ring:

$$Na_4Fe(CN)_6 + 11H_2SO_4 + 6H_2O \rightarrow FeSO_4 + 4NaHSO_4 + 6NH_4HSO_4 + 6CO\uparrow.$$

$$Na_3Fe(CN)_6 + 11H_2SO_4 + 6H_2O \rightarrow FeH(SO_4)_2 + \nearrow$$
$$3NaHSO_4 + 6NH_4HSO_4 + 6CO.$$

Chromates interfere because they form the yellowish orange of the dichromates in acid solution:

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2SO_4 + Na_2Cr_2O_7 + H_2O.$$

* * *

9. The solution is cooled to prevent the H_2SO_4 from acting too vigorously with the aqueous solution and to prevent loss of NO (which gives the test $FeSO_4.2NO$) from the solution.

* * *

10. Freshly prepared $FeSO_4$ is recommended because of the tendency of ferrous iron to oxidize slowly to the ferric condition in solution.

* * *

11. Mixing is prevented as far as possible so as to give a distinct boundary between the two solutions of different densities.

* * *

12. The reactions which give the nitrate test are as follows:

$$NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4.$$
$$2HNO_3 + 6FeSO_4 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 +$$
$$4H_2O + 2NO.$$
$$FeSO_4 + 2NO \rightarrow FeSO_4.2NO.$$

The composition of $FeSO_4.2NO$ is not definitely known and is variously reported. It would be safer to represent it $(FeSO_4)_x(NO)_y$.

* * *

13. Oxidizing agents such as chromates and iodides impair the delicacy of the borate test by destroying the turmeric. HNO_3 is an exception. These interfering substances may be removed as recommended in the test for nitrates (see Note **8,** this section).

14. The reaction for the formation of methyl (or ethyl) borate is as follows:

$$Na_2B_4O_7 + 3H_2O \rightleftarrows 2NaBO_2 + 2H_3BO_3.$$
$$3CH_3OH + H_3BO_3 + (H_2SO_4) \rightarrow (CH_3)_3BO_3 + 3H_2O(H_2SO_4).$$

The H_2SO_4 merely acts as a dehydrating agent.

* * *

15. Trivalent arsenic in the form of arsenites gives a precipitate of As_2S_3 readily, whereas in the form of arsenates in dilute acid solution, the arsenic is precipitated very slowly by H_2S (see Note **4**, p. 56).

If the precipitate for arsenites is not of a characteristic yellow color, it should be confirmed for As by procedure (**12**). Some of the amphoteric elements which have colored sulphides, such as Sb and Cu, might be sufficiently dissolved by the alkaline Na_2CO_3 to give precipitates that would obscure the light lemon-yellow of As_2S_3.

* * *

16. The reaction for the precipitation of As_2S_3 from an arsenite is:

$$2Na_3AsO_3 + 3H_2S \rightarrow As_2S_3 + 6NaOH.$$

The NaOH is immediately neutralized in the acid solution.

* * *

17. The solution is made only slightly alkaline if arsenites are present because of the possibility of precipitating $Mg(AsO_3)_2$. If arsenites are not present the solution should be made distinctly alkaline with NH_4OH, since this makes the precipitation of $MgNH_4AsO_4$ more complete.

* * *

18. The white precipitate of $MgNH_4PO_4$ cannot be distinguished from $MgNH_4AsO_4$ by ordinary observation. The reactions for the formation of the arsenate are given in Note **4**, p. 70.

19. The formation of Ag_3AsO_4 is discussed in Note **8**, p. 71.

* * *

20. If arsenites are present in large quantity, they may be precipitated by the magnesia mixture as $Mg(AsO_3)_2$. This compound and $MgNH_4PO_4$ are both converted to their respective yellow silver salts, Ag_3AsO_3 and Ag_3PO_4, by $AgNO_3$. Since these might obscure small amounts of the dark red Ag_3AsO_4, it is advisable to convert all three to their respective acids (AgCl being precipitated), and reduce the H_3AsO_4 by means of HI to give free I_2. Phosphates and arsenites are not reduced by HI. The reactions are:

$Ag_3AsO_3 + 3HCl \rightarrow 3AgCl + H_3AsO_3$.
$Ag_3PO_4 + 3HCl \rightarrow 3AgCl + H_3PO_4$.
$Ag_3AsO_4 + 3HCl \rightarrow 3AgCl + H_3AsO_4$.
$2KI + 2HCl \rightarrow 2KCl + 2HI$.
$H_3AsO_4 + 2HI \rightarrow H_3AsO_3 + H_2O + I_2$ (dissolves in CCl_4)

Equations on Group 3 Acid Radicals

NITRITES

1. Aluminum (turnings) and sodium hydroxide.
2. Sodium nitrite, water, and hydrogen (active).
3. Sodium nitrite and hydrochloric acid.
4. Nitrous acid and heat.
5. Nitric oxide and oxygen (atmospheric).
6. Nitrogen tetroxide, water, and potassium iodide.
7. Iodine and starch (no reaction).
8. Sodium nitrite and ammonium chloride (heated).

NITRATES

1. Aluminum (turnings) and sodium hydroxide.
2. Sodium nitrate, water, and hydrogen (active).
3. Sodium nitrate, concentrated sulphuric acid, and ferrous sulphate.

BORATES

1. Sodium tetraborate water, methyl alcohol (in the presence of concentrated H_2SO_4).
3. Sodium tetraborate and turmeric (complex reaction, no equation).

ARSENITES

1. Sodium arsenite and hydrogen sulphide.

ARSENATES

1. Sodium arsenite, ammonium hydroxide, and magnesium nitrate.
2. Sodium arsenate, ammonium hydroxide, and magnesium nitrate.
3. Magnesium ammonium arsenate and silver nitrate.
4. Magnesium ammonium arsenate and hydrochloric acid.
5. Arsenic acid, hydrochloric acid, and potassium iodide.
6. Iodine and carbon tetrachloride (no reaction).

Questions on Group 3 Acid Radicals

(See also *Theory*, pp. 168–174.)

1. Why are the Group 3 acid radicals not precipitated as a group and analyzed?
2. Why is the test for nitrites and nitrates with Zn made in an alkaline solution rather than in an acid solution?
3. What acid radicals interfere with this Zn-H_2 test for nitrites and nitrates? How do they interfere? Write the equations.
4. Why should nitrites be removed before testing for nitrates?
5. If nitrites were found in a solution, would you expect to find nitrates too? Why, or why not?
6. Why should the solution not be boiled in making the test for nitrites?
7. What other radicals (metallic and acid) interfere with the test for nitrates? In what way does each interfere? How are they removed?

8. Why should the solution be cooled upon addition of concentrated H_2SO_4 in making the test for nitrates?
9. Why should $FeSO_4$ used in the nitrate test be freshly prepared? What is the advantage in using $FeSO_4.(NH_4)_2SO_4.6H_2O$?
10. What types of radicals interfere with the turmeric test for borates?
11. What is the purpose of the concentrated H_2SO_4 in the methyl alcohol test for borates?
12. Under what conditions might the tests for arsenites and arsenates be omitted?
13. What is the basis of the separation of arsenites from arsenates by means of H_2S?
14. Why should the presence of arsenites be confirmed if the color of the precipitate is not a pure yellow?
15. What acid radicals might interfere with the test for arsenates? Why are two confirmatory tests sometimes necessary for arsenates?

DETECTION OF CARBONATES AND SULPHIDES

Since Na_2CO_3 is added in the preparation of the solution for acid radical analysis, the test for carbonates should be made on the original substance.

As stated in Note **2**, p. 147, many of the metallic sulphides ① are not decomposed by boiling with Na_2CO_3. Therefore, if the regular procedure for acid radicals indicates the absence of sulphides, they should be tested for either on the original substance or on the residue ② from the treatment with Na_2CO_3. (See (**36**) and Note **2**, p. 147.)

(**59**) **Detection of Carbonates.** — Using a side-neck test-tube, or a small distilling flask, arrange an apparatus such as is shown in Figure **7**. The delivery tube is to be fastened into the receiving tube by a two-holed stopper ③ and should dip well below the surface of 5 c.c. of almost saturated $Ba(OH)_2$ in that tube. In the side-neck test-tube or distilling flask place $\frac{1}{2}$ g. of the original substance. Stopper the tube or flask with a two-holed stopper containing the delivery tube and a safety-funnel. Pour 5 c.c. of dilute HCl (which has been previously boiled) ④ onto the solid by means of the safety-funnel, making sure that the end of the latter dips below the surface of the HCl ⑤. (If sulphites were found present add 3 c.c. of H_2O_2 ⑥ to the HCl.) Warm the mixture gently so that any escaping gas ⑦ passes through the $Ba(OH)_2$. If a white precipitate ⑧ has formed in the $Ba(OH)_2$ add $HC_2H_3O_2$ ⑨ drop by drop until the solution is just acid. If the precipitate is dissolved partially or entirely, the presence of **Carbonates** is indicated, and the precipitate is $BaCO_3$.

(60) Detection of Sulphides. — If **(38)** failed to show a test for sulphides, and sulphites, thiocyanates, nitrites, nitrates, and chromates were shown to be absent ⑩, test the original substance as directed in the next paragraph. If any or all of these radicals are known to be present, the residue from the treatment with Na_2CO_3 (see **[36]** and Note **2,** p. 147), is to be treated ⑪ as directed below rather than the original substance.

Using the apparatus for the carbonate test, put ½ g. of the original (or all the residue from **[36]**), in the distilling flask or tube and add a small piece (½ g.) of granulated or powdered zinc. Pour 5 c.c. of NaOH instead of $Ba(OH)_2$ in the receiving tube and submerge the latter in cold water contained in a beaker or dish. Close the apparatus and add 5 c.c. of HCl through the safety-funnel. Bring the solution slowly to boiling and distil the mixture gently for three to four minutes, or until about 3 c.c. of the distilled liquid has passed over into the receiving tube. The distillation should be carried out under a well-ventilated hood ⑫. Disconnect the receiving tube and add to the NaOH solution not more than ½ c.c. of $Pb(C_2H_3O_2)_2$ ⑬, shaking to redissolve the white precipitate which forms at first. A black precipitate indicates the presence of **Sulphides** and is PbS. (If the white precipitate persists, add NaOH little by little until it is dissolved ⑭).

NOTES ON THE CARBONATE AND SULPHIDE TESTS

1. Because of their insolubility, the sulphides of the Group 2 metals are not affected to any great extent by treatment with dilute HCl. Certain naturally occurring sulphides are also only slightly affected. By taking advantage of the reducing properties of the H_2 generated by Zn and HCl, these sulphides can be decomposed to a large extent, to give H_2S. On account of their great insolubility, this is true only to a limited extent for the

sulphides of arsenic, but this is of no consequence since those sulphides are appreciably soluble in Na_2CO_3 and would have been found in the regular acid radical procedure for sulphides.

* * *

2. The test for sulphides depends on the formation of H_2S in an acid solution. In the presence of such oxidizing agents as chromates, nitrites, and nitrates, H_2S might be completely oxidized and fail to give the test:

$$Na_2Cr_2O_7 + 8HCl + 3H_2S \rightarrow 2CrCl_3 + 7H_2O + 2NaCl + 3S.$$

$$2HNO_2 + H_2S \rightarrow 2H_2O + 2NO + S.$$

$$2HNO_3 + 3H_2S \rightarrow 4H_2O + 2NO + 3S.$$

* * *

In addition, sulphites and thiocyanates are reduced to H_2S by Zn and HCl, and might give the test for sulphides:

$$H_2SO_3 + 6H \rightarrow H_2S + 3H_2O.$$

$$HCNS + 2H \rightarrow HCN + H_2S.$$

Since all of these interfering radicals would have been metathesized and dissolved by treatment of the original with Na_2CO_3, the residue from that treatment may be safely tested for sulphides.

* * *

3. The receiving tube is stoppered to prevent, as far as is convenient, the admission of CO_2 from the air, which would give a slight turbidity in the $Ba(OH)_2$.

* * *

4. The HCl is boiled first to remove any dissolved CO_2 from the air, for the reason given in the previous note. Even with these precautions, a slight turbidity is frequently observed when carbonates are absent. Any very light precipitate after boiling for a reasonable time should be looked upon with suspicion.

5. This precaution is taken, obviously, to prevent the escape of any gas through the safety-funnel.

* * *

6. If sulphites are present, SO_2 will be evolved, and give a white precipitate of $BaSO_3$ with the $Ba(OH)_2$ solution. H_2O_2 is added to oxidize the sulphite before the SO_2 can be evolved:

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + \nearrow SO_2 \text{ (on warming)}.$$
$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2SO_3 \text{ (cold)}.$$
$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O.$$

* * *

7. The fact that most of the air in the distilling apparatus, etc., has to pass through the $Ba(OH)_2$ before the CO_2 reaches it, should be taken into account and the mixture therefore heated for a sufficient length of time. Too long heating on the other hand may cause a slight turbidity from CO_2 in the air (see Note **4** above). Experience will help to determine the length of time necessary for heating.

All carbonates are decomposed by the action of a dilute solution of a strong acid such as HCl, CO_2 being evolved:

$$MCO_3 + 2HCl \rightarrow MCl_2 + H_2O + \nearrow CO_2 \text{ (on warming)}.$$

* * *

8. The CO_2 evolved from the action of HCl on a carbonate, reacts with $Ba(OH)_2$ to form the insoluble $BaCO_3$:

$$CO_2 + Ba(OH)_2 \rightarrow BaCO_3 + H_2O.$$

The same thing is true of sulphites as indicated in Note **6** above:

$$SO_2 + Ba(OH)_2 \rightarrow BaSO_3 + H_2O.$$

* * *

9. $BaCO_3$ is distinguished from $BaSO_3$ by the fact that the latter is insoluble in dilute solutions of $HC_2H_3O_2$ whereas $BaCO_3$ is soluble, sulphurous acid being a stronger acid than carbonic. (See *Theory*, p. 116.)

10. See Note **2** above.

* * *

11. See Note **2** above.

* * *

12. Reduction of the sulphides or other compounds of arsenic and antimony by Zn and HCl may lead to the formation of arsine (AsH_3) and stibine (SbH_3), both of which are exceedingly poisonous gases not absorbed by $Ba(OH)_2$:

$$Na_3AsO_3 + 6H + 3HCl \rightarrow 3NaCl + 3H_2O + \nearrow AsH_3.$$

$$Sb_2O_3 + 12H \rightarrow H_2O + 2\nearrow SbH_3.$$

* * *

13. Since $Pb(OH)_2$ is an amphoteric hydroxide, that which is first precipitated by the addition of $Pb(C_2H_3O_2)_2$ to the NaOH solution is redissolved (if there is excess of NaOH present), to form sodium plumbite:

$$Pb(C_2H_3O_2)_2 + 2NaOH \rightarrow Pb(OH)_2 + 2NaC_2H_3O_2.$$
$$Pb(OH)_2 + 2NaOH \text{ (excess)} \rightarrow Na_2PbO_2 + 2H_2O.$$

* * *

14. More NaOH is added to dissolve the white $Pb(OH)_2$ in case there is not an excess already present. (See previous note.)

Equations for Carbonates and Sulphides

CARBONATES

1. Metallic carbonate (MCO_3) and hydrochloric acid (heated).
2. Carbon dioxide and barium hydroxide.

SULPHIDES

1. Zn and hydrochloric acid.
2. Metallic sulphide (MS) and hydrogen (active).
3. Hydrogen sulphide and sodium hydroxide.
4. Sodium sulphide and lead acetate.

Questions on the Tests for Carbonates and Sulphides

(See also *Theory*, pp. 168–174.)

1. Why is the test for carbonates always made on the original material?
2. What acid radical would interfere with the test for carbonates? How is this interference prevented?
3. Upon what two properties of H_2CO_3 does the detection of carbonates depend?
4. Could $Ca(OH)_2$ be used in place of $Ba(OH)_2$ in the carbonate test? Why is $Ba(OH)_2$ preferable? Could NaOH be used? Explain.
5. Why should a very faint test for carbonates be looked upon with suspicion? What is done to prevent this possibility?
6. Why are sulphides tested for in two places in the procedure?
7. Why would it not do just as well to pass H_2 from a generator through the solution in order to test for sulphides?
8. Why should the test for sulphides be conducted under the hood on occasions? Would any information obtained previously in the analysis indicate whether or not it was necessary to do the test for sulphides under the hood?
9. Why would it not do just as well to pass the gas into a solution of $Pb(C_2H_3O_2)_2$ directly, in the test for sulphides?
10. Could $Ba(OH)_2$ be used as well as NaOH as the absorbing medium for H_2S in the test for sulphides? Why is NaOH to be preferred?

SYSTEMATIC TREATMENT OF UNKNOWNS

General Remarks. — After the student has had sufficient practice in the analysis of "known" and "unknown" solutions and readily soluble substances, he may be given various samples of technical or mineral products for analysis. In general, most of these are not of a very complex nature, containing relatively few metallic and acid radicals. The chief difficulty, usually, is to get them into solution for analysis. In what follows, a procedure is given which will bring about the solution of most of the more common substances which are likely to occur in ordinary practice.

Preliminary Examination. — If the unknown substance be a solid it should be examined carefully and its general properties, such as color and odor, noted. Examination under a fairly strong lens will often determine whether the substance is homogeneous or a mixture.

The presence or absence of organic material ① (compounds of carbon other than carbonates) or water is to be noted. To do this, place a small sample (less than $\frac{1}{2}$ g.) in the bottom of a hard glass test-tube and heat it gently at first, finally igniting it strongly ②. Observe the formation of any moisture ③ or dark brown tarry deposit ④ on the sides of the tube; also whether the substance itself blackens ④ or emits any odor while heated ④. (*Smell cautiously!*) If organic matter is present it must be removed before the analysis for metals is begun. Treat a sample of the original by (**61**) for the removal of organic material. If organic material is absent, treat the original by (**62**), if it is an alloy, and by (**63**), if not.

A small sample of the original substance should be tested for the presence of ammonium by (**36**), unless it is an alloy.

(**61**) **Removal of Organic Material.** — If the previous procedure indicated the presence of organic material, bring a suitably sized sample (5 g. or less, depending on the amount of organic material indicated) into as finely divided form as is conveniently possible, and treat it with 5 c.c. of concentrated H_2SO_4 ⑤ (more if necessary) in a casserole. Heat slowly over a free flame until the substance is thoroughly charred. Allow the mixture to cool completely, and add concentrated HNO_3 ⑤ a little at a time (*caution! — under the hood*), stirring thoroughly after each addition, until rapid reaction ceases. Heat, gently at first, and then more strongly, keeping the dish in motion, until the substance is completely charred. Evaporate until the white fumes of SO_3 come off, and if the solution is not colorless ⑥ or almost so, cool, add more concentrated HNO_3 and repeat the evaporation. Continue this until the solution becomes light in color.

If the substance has dissolved completely ⑦, continue the evaporation to dryness. Cool thoroughly and dissolve the residue by boiling in 10 c.c. of H_2O. If the substance dissolves completely, treat the solution by (**1**), p. 43 (lead, barium and strontium are absent and need not be tested for in the regular metallic procedure). If a white residue ⑧ remains, filter and reserve the filtrate for (**1**). Wash the residue and treat it by (**64**).

If the treatment with H_2SO_4 has not dissolved the substance completely, continue the evaporation to dryness, and treat with H_2O as in the preceding paragraph. Filter from the residue, treating the solution by (**1**) and the washed residue by (**64**).

(**62**) **Treatment of Alloys.** — If the original substance is an alloy there will be no acid radicals present, though there

may be phosphorus, carbon, silicon, and sulphur. In addition the tests for Ca, Sr, Na, K, and NH_4 may also be omitted.

By means of a clean steel file or a knife, convert 0.5 g. of the alloy to a finely divided form and add 10 c.c. of dilute HNO_3 ⑩; cover the casserole with a watch glass and heat the mixture on a water bath as long as there is any evidence of action. Add a drop of conc. HNO_3 if the substance is not completely dissolved. If renewed action results, warm further and repeat the addition of HNO_3 until all action has ceased. Add a little H_2O if any crystals ⑪ are deposited. If the substance has dissolved completely, treat the solution by (**1**) for the detection of Group 1 metals. If the substance has not completely dissolved, evaporate to a bulk of 2–3 c.c. and add 5 c.c. of conc. HCl ⑫. If action is renewed by the addition of HCl, continue the heating on the water bath until it subsides, and then evaporate to dryness over a small flame. If the substance appeared to be an alloy of iron, heat this dry residue over a very small free flame until it is thoroughly dry, being careful not to ignite it. It is safer to conduct this drying operation in an oven for half an hour at 130° ⑬. If the original was not an alloy of iron ⑭ this drying may be omitted. Rub the residue ⑮ in the dish to a fine powder by means of a glass rod and add 5–10 c.c. of conc. HCl. Warm for several minutes, and if there is any further evidence of solution, evaporate *slowly* almost to dryness. Treat the wet residue with 2.5 c.c. of conc. HCl and 10 c.c. of H_2O. Heat the mixture to boiling and filter the boiling mixture. Wash with dilute HCl and then with hot water. Treat the residue by (**64**). Treat the filtrate by (**4**).

(**63**) **Treatment of Non-metallic Substances.** — If the original substance is free from organic material, it may be treated directly by the following procedure; but if organic material is present, it must first be removed as directed in (**61**).

Using an agate mortar, if available, grind a sample of the substance, free from organic material, to so fine a state that it feels like talcum powder to the touch. (A few extra minutes spent in grinding may save hours of time waiting for the substance to dissolve; proper pulverization is very important.) Take 1 g. of this sample and boil it with 10 c.c. of H_2O. If the substance dissolves completely, test the solution with litmus. If it is neutral or slightly acid, treat it directly by (**1**) for the detection of the metallic radicals. If the solution is alkaline, add HNO_3 until it is slightly acid and treat by (**1**) if no precipitate results. At the same time take note of the odor (*carefully!*) ⑯, the formation of any gas, etc. If the substance does not completely dissolve in H_2O, acidify the mixture with HNO_3 and then add a 5 c.c. excess and heat the solution to boiling. Maintain the solution just below the boiling temperature for several minutes, preventing evaporation as far as possible. If the substance has dissolved completely ⑰ on cooling, treat the solution by (**1**).

If the solid is not completely soluble in the hot acid ⑱, evaporate to 2–3 c.c., add 5 c.c. of conc. HCl, and evaporate to dryness, taking care not to ignite. Heat the dry residue over a small flame, or better in an oven, to 130°. Powder the residue in the dish, treat it with 5 c.c. HCl, and evaporate to dryness again. If the residue seems to be slowly dissolving as the evaporation proceeds, add 5 c.c. of conc. HCl and continue the evaporation slowly (best over a water bath) almost to dryness. Boil the wet residue with 10 c.c. of HCl and filter ⑲ while boiling. Treat the filtrate by (**4**). Wash the residue with equal parts of HCl and H_2O and finally with hot H_2O. Treat it by (**64**).

(**64**) **Fusion of the Acid Insoluble Residue with Sodium Carbonate.** — Tear away such parts of the filter paper containing the residue from (**63**) as have no residue upon them.

Roll the remainder in a platinum spiral inserted in a glass rod, and incinerate the paper and residue in the oxidizing portion of the flame. Allow any falling ash or residue to drop into a 30 c.c. nickel (20) crucible. Mix the ash and residue in the crucible thoroughly with 5–15 c.c. of a mixture of equal parts of solid Na_2CO_3 and K_2CO_3 (21): the quantity of the latter used should be at least twice the volume of the residue. Using a blast lamp or a powerful burner, heat the mass strongly until it fuses and continue this fusion for fifteen to twenty minutes (22). If possible, the crucible should be surrounded by an asbestos or clay chimney to get the maximum temperature. If any dark spots or particles are seen in the melt, add a few crystals of solid KNO_3 (23) at a time and continue to heat. After the fusion is complete, cool the crucible and its contents thoroughly, and if possible remove (24) the solid from the crucible. This may sometimes be accomplished by rolling the crucible between the palms of the hands and pressing so as to loosen the solid from the sides of the crucible by slightly distorting the shape of the latter. If the solid is removed, grind it to a fine powder in a mortar and boil it with 50 c.c. of H_2O until no further solution takes place. If the solid cannot be removed from the crucible, place the crucible and all in 50 c.c. of H_2O in a beaker and boil it until the mass is completely disintegrated and no further solution takes place. Filter from any residue (25) in either case, and wash the residue thoroughly. Divide the aqueous extract into two equal portions and treat one half by (**37**) *et seq.* for the acid radicals. Treat the other portion as directed below.

To the residue obtained in the past paragraph, add 10 c.c. H_2O and 5 c.c. of HNO_3 and boil in a casserole until no further solution takes place. Filter and discard (26) any undissolved residue. To 2 c.c. of this filtrate (27) add 5 c.c. of the filtrate from the hot-water treatment above. If no precipitate forms, combine the whole of the two filtrates from

the HNO_3 and H_2O treatments and proceed as directed below. If a precipitate does form, discard this test portion and treat the remainder of the solutions from the HNO_3 and H_2O separately as directed below.

To the combined HNO_3 and H_2O filtrates, or to each separately, add 5 c.c. conc. HCl (28) and filter. Test the precipitate by (2) and (3) for Ag and Pb. Evaporate the filtrate to dryness and warm to 130° as directed in (63). To the residue, add 2.5 c.c. of conc. HCl and 10 c.c. of H_2O. Boil and filter. Treat the filtrate by (4), for the remaining metallic radicals. Test the residue for silica (29) as follows: Make a Na_2CO_3 bead on the loop of a platinum wire and allow it to cool. Scrape some of the residue onto the bead, being careful not to get any filter paper fibers on the bead if possible. Heat the bead and residue in the outside edge of the flame, watching the bead carefully when it becomes molten. The presence of Silica is indicated by the formation of small bubbles of CO_2 in the molten bead.

(65) **Treatment of Solutions.** — If the original substance is a solution, test it for alkalinity or acidity with litmus paper. If the solution is distinctly alkaline, the tests for many of the metallic elements may be omitted (see the solubility tables in the Appendix). If the solution is acid, make it just alkaline with NH_4OH and evaporate a weighed portion of it to dryness to determine the percentage of solids as directed in (36b). Treat a portion of the residue by (61) for the detection of organic material.

If organic material is present, evaporate to dryness such a volume of the original as contains 1 g. of solid, and treat it by (61) for the removal of organic material.

If organic matter is absent, treat such a volume of the original solution as contains 1 g. of solid with HNO_3 or NH_4OH to make it neutral, and then slightly acidify with HNO_3. If a precipitate is formed, treat the whole of the

mixture by (**63**), (**64**) if necessary. If there is no precipitate, treat the solution by (**1**) *et seq.* for the detection of the metallic radicals.

Reserve a portion of the original solution for the detection of acid radicals as directed in (**36b**).

Test a portion of the solution for $\underset{\sim}{N}H_4$, p. 134.

Test a 10 c.c. portion of the original (if it is alkaline or neutral) for carbonates by acidifying with HCl and proceeding according to (**59**).

NOTES ON THE SYSTEMATIC TREATMENT OF UNKNOWNS

1. It is desirable to note the presence or absence of organic material because of its effect upon the regular metallic procedure. If tartrates, oxalates, sugars, etc., are present, they affect the precipitation of the metals in Group 3 particularly. Thus, tartrates, by formation of complex ions with Al and Cr, prevent the precipitation of these two metals as hydroxides. In addition the organic materials interfere in general with the processes of precipitation, filtration, etc., so that it is better to remove them before analyzing for the metals.

* * *

2. The ignition in a closed tube very frequently gives helpful information as to what may be looked for later. Thus, As_2O_3, Sb_2O_3, HgCl, $HgCl_2$, and NH_4 salts, in addition to certain organic materials, give a white sublimate in the tube. HgO and As_2S_3 form yellow sublimates (the former accompanied by globules of Hg). Free S and the polysulphides give red-brown drops which cool to yellow, as sublimate. This is accompanied by the odor of SO_2. A violet vapor indicates the presence of free I_2 or iodides in the presence of an oxidizing agent. A brown gas may indicate the presence of nitrites or bromides in the presence of an oxidizing agent. A colorless gas may indicate peroxides, chlorates, oxides, nitrates, carbonates,

oxalates, or organic material. The last three form CO_2 which will turn a drop of $Ba(OH)_2$ on a glass rod, turbid. The others evolve O_2, which may be detected by the familiar ignited splint test.

* * *

3. Water condensing on the cool sides of the tube may come from the decomposition of organic material containing H_2, or from hydrates such as $CuSO_4.5H_2O$, or from inorganic compounds containing H_2 and O_2, such as $NaHSO_4$.

* * *

4. Unless the blackening in the tube is accompanied by a tarry deposit, it probably does not come from any organic matter, because many inorganic substances (nitrates of the heavy metals) blacken (form oxides) on heating.

* * *

5. Treatment with hot concentrated H_2SO_4 and HNO_3, by virtue of the decomposing action of the former and the oxidizing action of both (chiefly HNO_3), will bring about the destruction of almost any organic material, even the most inert, with the formation of CO_2, H_2O, etc.

* * *

6. The dark brown material indicates that the carbonaceous material is not completely oxidized, so that the oxidation is continued until the brown color is no longer in evidence.

* * *

7. Complete solution in hot concentrated H_2SO_4 indicates the absence of silicates and silica. Although silicic acid is soluble (colloidally) in strong acids under certain conditions, it is dehydrated to form SiO_2 by the hot concentrated H_2SO_4. The dehydrated SiO_2 is insoluble. Concentrated H_2SO_4 would interfere with the conduct of the metallic radical procedure and is therefore removed by evaporation.

8. A white precipitate or residue may be due to the insoluble sulphates of Pb, Ba, Sr, and Ca, which are brought into solution later by fusion with Na_2CO_3 (see Note **22** below).

* * *

9. In addition to the silicates and sulphates mentioned in the two previous notes, the sulphates of Cr (dehydrated by $\frac{conc}{\Delta}H_2SO_4$), Sb, Sn, and Bi are only partially dissolved by H_2SO_4.

* * *

10. All of the substances commonly found in alloys are dissolved by boiling HNO_3, except Sb, Sn, Si, and C. The first three are oxidized to form, respectively, $Sb_2O_5.nH_2O$, $SnO_2.nH_2O$, and $SiO_2.nH_2O$:

$$3Sn+4HNO_3+3nH_2O \rightarrow 3SnO_2.nH_2O \downarrow +4NO+H_2O, \text{ etc.}$$

* * *

11. The nitrates of some of the elements may be precipitated if these elements are present in relatively large quantity. This is particularly true of the nitrate of lead.

* * *

12. The addition of HCl serves two purposes: in the first place, it has a greater solvent action on some of the metals than HNO_3. Thus, in the case of Al, HNO_3 tends to form a protective coat of Al_2O_3 on the surface of the Al and hinder further action of the acid. Secondly, the HNO_3 oxidizes the HCl to form aqua regia, which contains active chlorine and nitrosyl chloride and has a much greater solvent action than either one of the acids alone:

$$HNO_3 + 3HCl \rightarrow 2H_2O + NOCl + 2Cl.$$
$$NOCl + HOH \rightarrow HNO_2 + HCl.$$
$$Cl_2 + HOH \rightarrow HCl + HOCl.$$

The energy of the decompositions of HClO and NOCl, together with the formation of HNO_2, makes aqua regia a much more energetic oxidizing agent than HNO_3 alone.

The oxides of Sn and Sb are dissolved by the HCl in the aqua regia, but AgCl and $PbCl_2$ are precipitated:

$SnO_2.nH_2O + 4HCl \rightarrow SnCl_4 + (n + 2)H_2O.$
$Sb_2O_5.nH_2O + 10HCl \rightarrow 2SbCl_3 + 2Cl_2 + (n + 5)H_2O.$

* * *

13. Silicic acid, $SiO_2.nH_2O$, as stated before, is colloidally soluble in strong acids, but if heated for a reasonable length of time at 130°, it is dehydrated to form SiO_2 which is quite insoluble in acids. If the silicic acid were not removed, it might, if it did not precipitate sooner, appear in the test for Al and, since it looks very much like $Al(OH)_3$, cause confusion in determining the presence of that element.

* * *

14. The alloys of iron are the only ones likely to contain Si, so that the dehydration is generally unnecessary unless the original appears to be an iron product.

* * *

15. The residue may consist of SiO_2, AgCl, $PbCl_2$, or certain special alloys, such as Duriron (a ferrosilicon alloy), which are not readily attacked by aqua regia.

* * *

16. As in the closed-tube treatment, the presence of certain things may be indicated by the action of HNO_3 on the original substance. Thus, CO_2, H_2S, HCN, NO_2, I_2, Br_2, etc., might be liberated at this point.

* * *

17. If solution is complete at this point, the substances mentioned in Note **18** below, are absent.

* * *

18. The following are the more common substances which are insoluble in HNO_3: $SnO_2.nH_2O$, $Sb_2O_5.nH_2O$, $SiO_2.nH_2O$, the native and ignited oxides of these elements along with those of Al and Cr, anhydrous Cr salts, PbO_2 and MnO_2, ignited $PbCrO_4$ and $BaCrO_4$,

$PbSO_4$, $BaSO_4$ and $SrSO_4$, the silicates and sulphides of many elements, the halides of Ag, the phosphate and arsenate of Sn, S, C, and SiC.

On subsequent treatment with HCl, the aqua regia formed dissolves the sulphides not already dissolved by HNO_3, along with the hydrated oxides of Sn and Sb. (Cassiterite, native SnS_2, is not dissolved by aqua regia.) The solution is evaporated to dehydrate the $SiO_2.nH_2O$ and to remove HNO_3, since the HCl alone has a better reducing and solvent effect on such substances as PbO_2, MnO_2, and the phosphate and arsenate of Sn. The treatment with HCl is carried out slowly, so that the slowly dissolving oxides such as $SnO_2.nH_2O$ and Cr_2O_3 may have a chance to dissolve.

* * *

19. If there is no residue at this point, Ag, Si, and SiO_2 are absent. Any residue might consist of these three, in addition to many of the substances mentioned in Note **18,** which are insoluble in HCl, HNO_3, or a mixture of the two. Such substances are: C, S, the halides of Ag, the sulphates of Ba, Sr, Ca, and Pb, ignited or anhydrous chromic salts, chromite, ($Fe[CrO_2]_2$), CaF_2, and certain silicates. Native or ignited Cr_2O_3, Al_2O_3, and SnO_2 dissolve only partially in HCl.

* * *

20. A nickel crucible is recommended because it is attacked only slightly by an alkaline flux. Some Ni is dissolved, however, and therefore the test for that element in the regular procedure must be omitted. The same is true, of course, of the tests for Na and K, since they are introduced with the flux. When the metals of Groups 1 and 2 are known to be absent, it is advisable to use a platinum crucible so that the Ni test need not be omitted. Since the compounds of Groups 1 and 2 metals are easily reducible to the free metal, there is danger that the platinum might be damaged by alloying with these metals at high temperatures.

21. A mixture of Na_2CO_3 and K_2CO_3 is used because it melts at a lower temperature than either of the carbonates alone.

* * *

22. The fusion is continued for an extended period of time because the reactions in the molten state do not take place as readily as in solution.

The alkali carbonates play a double rôle in the process of fusion. In the first place they metathesize such compounds as $PbSO_4$, $BaSO_4$, and metal silicates, insoluble in acids, to soluble sodium salts and acid soluble carbonates. In addition, they supply a basic oxide, Na_2O (not as such) which combines with certain amphoteric oxides (MnO_2, Al_2O_3, etc.) to form soluble sodium salts. Certain silicates are rendered more soluble ("opened up") by the increase in the ratio of the basic oxide (Na_2O) to the acidic oxide, because the insolubility of complex silicates seems to increase with decreasing ratio of acidic oxide to basic.

Some of the typical reactions of the fusion are:

$$MSiO_3 + Na_2CO_3 \rightarrow Na_2SiO_3 + MCO_3.$$

$$PbSO_4 + Na_2CO_3 \rightarrow PbCO_3 + Na_2SO_4.$$

$$4AgCl + 2Na_2CO_3 \rightarrow 4Ag + 4NaCl + 2CO_2 + O_2.$$

$$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2.$$

$$MnO_2 + Na_2CO_3 + O(KNO_3) \rightarrow Na_2MnO_4 + CO_2.$$

* * *

23. The reason for the addition of KNO_3 is indicated in the last equation of the previous note. The oxides of Cr, Mn, etc. dissolve readily in the higher state of oxidation, forming chromates and manganates, whereas in the lower state they are not attacked by the Na_2CO_3:

$$2KNO_3 \rightarrow 2KNO_2 + O_2.$$

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \rightarrow 4Na_2CrO_4 + 4CO_2, \text{ etc.}$$

24. The solid is removed from the crucible if possible so that it may be pulverized and in this condition be dissolved much more readily than if it were in one solid mass.

* * *

25. This residue may consist of the carbonates and oxides of the metals which do not show amphoteric character, e.g. Fe_2O_3, $PbCO_3$, $BaCO_3$, $SrCO_3$. The majority of these are acid soluble. The solution obtained by the water extraction will contain the sodium salts of the amphoteric metals, e.g. Na_3AsO_3, $NaAlO_2$, and Na_2MnO_4, in addition to the sodium salts of the acid radicals, such as Na_2SO_4 and NaCl, and Na_2SiO_3 from the decomposition of the silicates.

* * *

26. Some of the silicates and native oxides are only partially decomposed on fusion with Na_2CO_3 but enough is got into solution by the procedure recommended to give a distinct test for them.

* * *

27. When such substances as $BaSO_4$ and $PbSO_4$ are absent, the solution from the water extraction and that from the HNO_3 extraction may be mixed without the formation of a precipitate and the whole analyzed at once rather than the two solutions separately. If any of these compounds are present, $BaSO_4$ for example, then the HNO_3 solution would contain $Ba(NO_3)_2$ from the solution of $BaCO_3$ and would give a precipitate with the Na_2SO_4 from the water extraction. (See the equations in Note **24** above.)

* * *

28. The filtrate or filtrates are evaporated with HCl to dehydrate the SiO_2 (see Note **18** above) and at the same time to remove HNO_3 since, with the exception of AgCl and $PbCl_2$, which are precipitated, the residue of chlorides is more soluble than when in the form of nitrates.

29. The test for SiO_2 depends on the fact that the latter is able to displace the CO_2 from Na_2CO_3:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + \overset{\nearrow}{CO_2}.$$

* * *

30. Since an original unknown solution may be of any concentration, it is advisable to evaporate it so that sufficient may be used to give a dependable analysis. The solution is neutralized if acid, to form ammonium salts and thereby prevent the loss of volatile acids during the evaporation. Also to bring about evaporation more readily in case free H_2SO_4 or H_3PO_4 be present, since they boil above 300°.

APPENDICES

APPENDIX I

REAGENTS

Acids and Bases

Substance	*Normality (app.)*	*Sp. Gr.*	*Amounts*	
			Reagent	*Water*
Acetic acid.....	6	1.042	350 c.c.	650 c.c.
Hydrochloric acid.....	12	1.19	1000 c.c.	—— c.c.
Hydrochloric acid.....	6	1.11	500 c.c.	500 c.c.
Nitric acid.....	16	1.42	1000 c.c.	—— c.c.
Nitric acid.....	6	1.19	380 c.c.	620 c.c.
Sulphuric acid.....	36	1.84	1000 c.c.	—— c.c.
Sulphuric acid.....	18	1.49	500 c.c.	500 c.c.
Sulphuric acid.....	6	1.18	170 c.c.	830 c.c.
Ammonium hydroxide..	15	0.90	1000 c.c.	—— c.c.
Ammonium hydroxide..	6	0.92	400 c.c.	600 c.c.
Barium hydroxide (sat.)	0.35	——	30 g.	1000 c.c.*
Potassium hydroxide...	6	1.26	340 g.	1000 c.c. (*ca.*)†
Sodium hydroxide.....	6	1.22	250 g.	1000 c.c. (*ca.*)‡

* Shake 1000 c.c. of H_2O with $Ba(OH)_2.8H_2O$ at ordinary temperature and filter.

† Dissolve 340 g. of the best c.p. KOH in an amount of H_2O less than a liter, and then dilute to a liter.

‡ Dissolve 250 g. of the best (crystallized from alcohol) NaOH in an amount of H_2O less than a liter and then dilute a liter.

REAGENTS

Salts*

Name of Salt	*Formula of Salt*	*Normality*	*Formula Weight*	*Grams/Liter*
Ammonium acetate....	$NH_4C_2H_3O_2$	3	77	250
Ammonium acetate....	$NH_4C_2H_3O_2$	12	77	1000
Ammonium chloride...	NH_4Cl	3	54	165
Ammonium oxalate†...	$(NH_4)_2C_2O_4.H_2O$	0.3	142	(sat.)
Ammonium nitrate....	NH_4NO_3	1	80	80
Ammonium sulphate...	$(NH_4)_2SO_4$	1	132	132
Barium chloride.....	$BaCl_2.2H_2O$	1	244	122
Calcium chloride‡.....	$CaCl_2.6H_2O$	1	219	110
Cobalt nitrate.....	$Co(NO_3)_2.6H_2O$	0.2	291	30
Ferric chloride.....	$FeCl_3.6H_2O$	1	270	90
Ferric nitrate.....	$Fe(NO_3)_3.9H_2O$	1	404	135
Lead acetate.....	$Pb(C_2H_3O_2)_2.3H_2O$	1	379	190
Lead nitrate.....	$Pb(NO_3)_2$	1	331	165
Mercuric chloride.....	$HgCl_2$	0.2	271	25
Nickel nitrate.....	$Ni(NO_3)_2.6H_2O$	1	291	145
Potassium chromate...	K_2CrO_4	3	194	285
Potassium cyanide.....	KCN	1	65	65
Potassium ferricyanide.	$K_3Fe(CN)_6$	1	329	110
Potassium ferrocyanide.	$K_4Fe(CN)_6.3H_2O$	1	422	105
Silver nitrate.....	$AgNO_3$	1	170	170
Sodium carbonate.....	Na_2CO_3	3	106	160
Sodium nitrite.....	$NaNO_2$	1	69	70
Sodium secondary phosphate.....	$Na_2HPO_4.12H_2O$	1	358	120
Sodium sulphite.....	$Na_2SO_3.7H_2O$	1	252	125

* This table contains salts which do not require any special preparation. Merely dissolve the quantity specified in the column headed *grams/liter* in a quantity of water less than a liter and then dilute to a liter.

† Make a saturated solution by warming 50 g. of the salt with a liter of water, cool, allowing sufficient time for crystallization, and decant.

‡ This solution should be freed from sulphate if there is any present. This may be done by treating each liter with 10 c.c. of the $BaCl_2$ solution, allowing the mixture to stand, and filtering.

REAGENTS

Which Require Special Preparation

Aluminon (see Hammett and Sottery, *J. Am. Chem. Soc.*, 47:142).

Ammonium Carbonate, 6*N*. Dissolve 250 g. of $(NH_4)_2CO_3$ which has been recently ground, in a volume of cold 6*N* NH_4OH which is less than a liter, and then dilute to a liter with 6*N* NH_4OH.

Ammonium Molybdate. Dissolve 90 g. of commercial ammonium molybdate (pure) $(NH_4)_6Mo_7O_{24}.4H_2O$ in 200 c.c. of 3N NH_4OH, add 250 g. of NH_4NO_3 and dilute to a liter with H_2O.

Bromine Water. Dissolve 100 g. KBr in a liter of water, add 10 c.c. of Br_2, and shake until the Br_2 dissolves.

Chlorine Water. Saturate water with Cl_2 gas (under the hood). Keep in a brown glass bottle.

Chloride Reagent (0.25 *N* NH_4OH, 0.01 *N* $AgNO_3$, 0.25*N* KNO_3). Dissolve 1.7gm. of $AgNO_3$ and 25 g. of KNO_3 in an amount of water less than a liter, add 17 c.c. of concentrated NH_4OH, and dilute to a liter.

Dimethylglyoxime, 0.1*N*. Dissolve 10 g. of the solid in 1000 c.c. of 95 per cent C_2H_5OH.

Ferrous Chloride, 1*N*. Dissolve 65 g. of $FeCl_2$ in an amount of 0.5N HCl less than a liter, dilute the solution to a liter with 0.5N HCl, and keep in contact with iron nails.

Hydrogen Peroxide. Use the 3 per cent hydrogen peroxide of commerce.

Magnesia Mixture (1*N* $Mg(NO_3)_2$, 3*N* $NH_4NO_3 + NH_4OH$). Dissolve 130 g. of $Mg(NO_3)_2.6H_2O$ and 240 g. of NH_4NO_3 in an amount of water smaller than a liter, add 10 c.c. of conc. NH_4OH, and dilute to a liter.

Nitroso-beta-Naphthol. Dissolve 0.5 g. of alpha-nitroso-beta-naphthol ($C_{10}H_6$[OH]NO) by boiling with 100 c.c. H_2O and 5 c.c. of dilute (2*N*)NaOH, filter from any undissolved material, and dilute the filtrate to a liter with H_2O. (A solution prepared in this manner ought to keep for a year at least. See *J. Soc. Chem. Ind.*, 34: 641 [1915].)

Potassium Mercuri-Iodide (0.5*N* in K_2HgI_4, 3*N* in NaOH). Dissolve 115 g. of HgI_2 and 80 g. of KI in an amount of water less than 500 c.c. Dilute to 500 c.c. with H_2O, add 500 c.c. of 6*N* NaOH, and filter from any precipitate formed. This solution should be preserved in a brown bottle.

Potassium Antimonate. Add 20 g. of the best commercial salt to a liter of boiling water, boiling until nearly all the salt has dissolved. Cool the mixture quickly, add 35 c.c. of 6*N* KOH, allow the mixture to stand for a day, and filter it.

Stannous Chloride, 1N. Dissolve 113 g. of $SnCl_2.2H_2O$ in 100 c.c. of concentrated HCl, dilute to a liter with H_2O, and keep in contact with granulated tin.

Turmeric. Shake an excess of turmeric with a liter of 95 per cent C_2H_5OH and filter from the excess.

SOLID REAGENTS

Aluminum turnings
Antimony powder
Borax
Iron powder or nails
Lead dioxide
Manganese dioxide
Potassium chlorate
Powdered quartz
Sodium carbonate (anhyd.)
Sodium nitrate
Sodium peroxide
Tin (granulated)
Zinc (powdered or finely granular)

OTHER REAGENTS

Carbon tetrachloride
Ethyl alcohol
Methyl alcohol (acetone free)

APPENDIX II

PREPARATION OF TEST AND STOCK SOLUTIONS FOR PRELIMINARY EXPERIMENTS AND UNKNOWNS

The following solutions should be prepared from chemicals of the highest degree of purity (preferably analyzed) which can be obtained. Since most of them occur in the form of fairly small crystals, it is usually not necessary to grind them further. The quantities recommended should be weighed out on a platform balance and dissolved in hot water, unless otherwise directed, in sufficient quantity to make the total volume one liter.

In some cases the salt is not sufficiently soluble to give solutions of the desired strength. These are marked (d). They contain 50 mg. per c.c. of the radical instead of 100 mg. per c.c., as is the case with most of the solutions.

The test solutions for the preliminary experiments should contain 10 mg. of the element per c.c. The stock solutions should therefore be diluted with nine times their own volume of distilled water. In the case of the more difficultly soluble substances (d) the stock solution should be diluted with only four times its own volume of distilled water.

The unknown solutions should be made to contain known amounts of the various radicals and the amounts varied at the discretion of the instructor. These amounts should be recorded and the student required to report approximate quantities of each radical found. In general the solutions should be so prepared as to contain a fairly large amount of one element, say 200 mg. per 10 c.c.; a moderate amount of a second, say 25 mg. per 10 c.c., and small amounts of two to five others (less than 5 mg.). These solutions may be conveniently prepared in 500 c.c. bottles by mixing 100 c.c. (10,000 mg.) of the first solution, 12.5 c.c. (1250 mg.) of the second, and say 2.5–3 c.c. (250–300 mg.) of the others, and filling the bottle with distilled water.

These solutions may be conveniently given to the student in 30 c.c. specimen bottles, one filling of which should be ample for retests, accidental losses of solution, etc., 10 c.c. being sufficient for any one analysis. The instructor should keep a record of each time the stock solutions and unknown solutions are refilled, in addition to a record of the students' reports of traces of calcium, magnesium, sodium, and potassium, etc., not intentionally put into the unknown solutions, but possibly present as impurity in the salts from which the solutions are prepared. Since these traces are likely to be variable in different solutions prepared from time to time, it is advisable to keep a record of the preparation of a fresh solution.

In addition to unknown solutions, the student should be given various samples of readily soluble solids containing mixtures of dry salts. The instructor may make these from such samples as NaCl, Na_2CO_3, K_2SO_4, $Fe_2(SO_4)_3$, and $CuSO_4.5H_2O$, — varying the percentages of the components at will.

Radical	*Formula of Salt*	*Gms./L.*
Silver	$AgNO_3$	157
Lead	$Pb(NO_3)_2$	160
Mercury (-ous)	$HgNO_3.H_2O$*	140
Mercury (-ic)	$Hg(NO_3)_2.\frac{1}{2}H_2O$	167
Bismuth	$Bi(NO_3)_3.5H_2O$†	233
Copper	$Cu(NO_3)_2.5H_2O$	380
Cadmium	$Cd(NO_3)_2.4H_2O$	278
Arsenic (-ous)	As_2O_3‡	33
Arsenic (-ic)	As_2O_5	153
Antimony	$SbCl_3$§	188
Tin (-ous)	$SnCl_2.2H_2O$‖	189
Tin (-ic)	$SnCl_4.3H_2O$‖	270

* Dissolve in N HNO_3.
† Dissolve in 3N HNO_3.
‡ Dissolve in 1 liter of 6N HCl → 25 mg./c.c.
§ Dissolve in 6N HCl, add HCl when diluting.
‖ Dissolve in 6N HCl.

Radical	*Formula of Salt*	*Gms/L.*
Aluminum	$Al(NO_3)_3.9H_2O$ (d)	700
Chromium	$Cr(NO_3)_3.9H_2O$	770
Iron (-ic)	$Fe(NO_3)_3.9H_2O$	715
Iron (-ous)	$FeCl_2$¶	230
Cobalt	$Co(NO_3)_2.6H_2O$	500
Nickel	$Ni(NO_3)_2.6H_2O$	500
Manganese	$Mn(NO_3)_2.6H_2O$	530
Zinc	$Zn(NO_3)_2.6H_2O$	455
Barium	$BaCl_2.2H_2O$	180
Strontium	$Sr(NO_3)_2$	242
Calcium	$Ca(NO_3)_2.4H_2O$	590
Magnesium	$Mg(NO_3)_2.6H_2O$ (d)	530
Potassium	KNO_3	257
Sodium	$NaNO_3$	371
Ammonium	NH_4NO_3	445
Ferrocyanide	$K_4Fe(CN)_6.3H_2O$	210
Ferricyanide	$K_3Fe(CN)_6$	155
Sulphide	$Na_2S.9H_2O$ (d)	375
Chloride	NaCl	165
Bromide	KBr	150
Iodide	KI	130
Thiocyanate	KCNS	170
Sulphate	$Na_2SO_4.10H_2O$	340
Sulphide	$Na_2SO_3.7H_2O$	315
Fluoride	KF	305
Chromate	K_2CrO_4	170
Oxalate	$K_2C_2O_4.H_2O$	210
Nitrite	$NaNO_2$	150
Nitrate	$NaNO_3$	140
Borate	$Na_2B_4O_7.10H_2O$	90
Arsenate	As_2O_5	85
Arsenite	$Na_4As_2O_5$	150
Phosphate	$Na_2HPO_4.10H_2O$ (d)	190

¶ Dissolve in 0.5 NHCl, keep in contact with Fe nails.

APPENDIX III

SOLUBILITY TABLES

Solubility Chart

	Acetate	*Arsenate*	*Arsenite*	*Borate*	*Bromide*	*Carbonate*	*Chlorate*	*Chloride*	*Chromate*	*Cyanide*	*Ferricyanide*	*Ferrocyanide*	*Fluoride*	*Hydroxide*	*Iodide*	*Nitrate*	*Oxalate*	*Oxide*	*Phosphate*	*Silicate*	*Sulphate*	*Sulphide*	*Tartrate*
Al	W	a	..	A	W	..	W	W	..	..	..	w	I	A	W	W	A	A	A	a	W	A	W
NH_4	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	..	W	..	W	W	W
Sb	..	a	A	..	w	..	..	w	A	..	..	..	W	..	w	..	A	A	w	..	w	A	A
Ba	W	A	A	A	W	A	W	W	A	w	w	w	a	W	W	W	A	W	A	A	I	W	A
Bi	W	A	..	A	w	A	W	w	A	w	..	w	A	A	A	W	A	A	A	..	W	A	A
Cd	W	A	..	w	W	A	W	W	A	A	A	..	w	A	W	W	A	A	A	A	W	A	w
Ca	W	A	A	w	W	A	W	W	w	W	W	W	a	w	W	W	A	w	A	A	A	W	A
Cr	W	A	..	A	W	..	W	W	A	A	..	..	W	A	W	W	w	A	A	A	W	A	W
Co	W	A	A	A	W	A	W	W	A	a	I	I	w	A	W	W	A	A	A	A	W	A	W
Cu	W	A	A	W	W	A	W	W	W	A	I	I	A	A	W	W	A	A	A	A	W	A	W
Au	..	..	..	..	W	..	..	W	..	A	..	..	..	A	A	..	..	A	..	..	..	A	..
H	W	W	..	W	W	..	W	W	..	W	W	W	W	W	W	W	W	W	W	W	w	W
Fe″	W	A	A	A	W	A	W	W	..	a	I	I	w	A	W	W	A	A	A	A	W	A	w
Fe‴	W	A	A	A	W	..	W	W	W	..	W	I	W	A	W	W	A	A	A	A	W	A	W
Pb	W	A	A	A	a	A	W	a	a	A	w	A	A	A	A	w	W	A	A	A	a	A	A
Mg	W	A	A	w	W	A	W	W	W	W	W	W	a	A	W	W	A	A	A	A	W	A	W
Mn	W	A	A	A	W	A	W	W	W	W	I	A	A	A	W	W	w	A	A	A	W	A	w
Hg′	w	A	A	..	a	A	W	a	A	A	..	..	W	..	A	W	A	A	A	..	w	A	w
Hg″	W	A	A	..	W	A	W	W	w	A	A	A	w	..	A	W	A	A	A	..	W	A	A
Ni	W	A	A	A	W	A	W	W	A	a	I	I	w	A	W	W	A	A	A	A	W	A	A
K	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Ag	w	A	A	A	I	A	W	I	A	I	I	I	W	..	I	W	A	A	A	..	w	A	A
Na	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Sn‴′	W	A	..	..	W	..	..	W	..	..	..	I	W	A	W	w	W	A	A	..	W	A	..
Sn″	W	A	A	A	W	..	W	W	A	..	..	I	W	A	W	..	A	A	A	..	W	A	A
Sr	W	A	A	A	W	A	W	W	w	A	W	W	a	A	W	W	A	w	A	A	a	W	A
Zn	W	A	A	A	W	A	W	W	W	A	A	I	w	A	W	W	A	A	A	A	W	A	A

W Soluble in water.
A Insoluble in water but soluble in acids.
w Sparingly soluble in water but soluble in acids.
a Insoluble in water and only sparingly soluble in acids.
I Insoluble in both water and acids.

From the above table the following general facts become evident:

1. That all potassium, sodium and ammonium salts are soluble in water.
2. That all acetates, bromides, chlorates, chlorides, iodides, nitrates, sulphates and thiocyanates (not in table) are soluble with such exceptions as are indicated in the table on page 217.
3. That all cyanides, ferrocyanides and ferricyanides are sparingly soluble or insoluble except for alkaline earth and alkali groups.
4. That all hydroxides are insoluble in water except the alkali group, $Ca(OH)_2$, and $Ba(OH)_2$. (These latter two are only somewhat soluble.)
5. That all sulphides are insoluble in water except those of the alkali and alkaline earth groups. They may be subclassified on the basis of their solubility in acids, which appears from the group definitions. The sulphides of Al and Cr are completely hydrolyzed by H_2O.

SOLUBILITY OF SOME "INSOLUBLE" SALTS IN WATER*

	Cl	Br	I	CNS	F	S	OH	CO_3	SO_4	CrO_4	C_2O_4
Ag	1.53	0.084	0.003	0.13		0.10	27	17	5500	25	35
Pb	9610	8340	613		700	0.86	75	1	43	0.2	1.5
Hg^I	0.5	0.04	0.0002								
Hg^{II}			60	696		0.013	51				
Ba					1600		37000	23	2.3	3.8	86
Sr					120		7700	11	110	1200	46
Ca					16		1700	13	2000	4000	5.6
Mg					76		15	800			300

The table gives the number of milligrams of the anhydrous salt that are held in solution by 1 liter (*i.e.*, 1,000,000 mg.) of water at 18–20°.

* Taken with permission from W. A. Noyes' *Qualitative Analysis* (Henry Holt and Co., 1923).

6. That all arsenates, arsenites, borates, carbonates, chromates, oxalates, phosphates, and sulphites except those of the alkali elements are insoluble in water but dissolve in dilute solutions of strong acids.

N.B. It is to be noted that these statements are general in their scope. Individual exceptions to these statements, where such exceptions do not include important compounds, have been left out of consideration.

THE SOLUBILITY PRODUCTS (K_{sp}) OF SOME INSOLUBLE SUBSTANCES* USED IN ANALYTICAL CHEMISTRY
(AT ROOM TEMPERATURE)

Salt	K_{sp}	*Salt*	K_{sp}
Silver bromide	4.0×10^{-13}	Mercuric sulphide	4.0×10^{-53}
Silver carbonate	5.0×10^{-12}	Mercurous chloride	3.1×10^{-18}
Silver chloride	1.1×10^{-10}	Magnesium carbonate	2.0×10^{-4}
Silver chromate	2.0×10^{-12}	Magnesium hydroxide	1.2×10^{-11}
Silver cyanide	2.0×10^{-12}	Magnesium ammonium phosphate	2.5×10^{-13}
Silver dichromate	2.0×10^{-7}	Magnesium oxalate	8.6×10^{-5}
Silver hydroxide	2.0×10^{-8}		
Silver iodide	1.0×10^{-16}	Lead carbonate	3.3×10^{-14}
Silver sulphide	1.6×10^{-49}	Lead chromate	1.8×10^{-14}
Silver thiocyanate	1.0×10^{-12}	Lead sulphate	1.0×10^{-8}
		Lead sulphide	1.0×10^{-29}
Barium carbonate	7.0×10^{-9}		
Barium chromate	2.0×10^{-10}	Strontium carbonate	1.6×10^{-9}
Barium oxalate	1.7×10^{-7}	Strontium oxalate	5.0×10^{-8}
Barium sulphate	1.0×10^{-10}	Strontium sulphate	2.8×10^{-7}
Calcium carbonate	1.2×10^{-8}		
Calcium fluoride	3.5×10^{-11}		
Calcium sulphate	6.1×10^{-5}		
Calcium oxalate	2.0×10^{-9}		
Cadmium sulphide	4.0×10^{-29}		
Cupric sulphide	0.5×10^{-45}		

*See also *Theory*, p. 107.

APPENDIX IV

DEGREE OF IONIZATION

AT 20° C. APPROXIMATELY

The following tables give the degree of ionization in round numbers for the common acids, bases and salts, at room temperature. In the case of strong electrolytes, of course, the numbers express only the apparent degrees of ionization. All data are expressed in per cent and are given for normal and normal/10 solutions wherever such data could be readily obtained.

	Strong			Moderate		Weak				
	Ions	*N*	*N/10*	*Ions*	*N/10*	*Ions*	*N*	*N/10*	*Ions*	*N/10*
A	$H^+NO_3^-$	82	90	$H^+SO_4^{=}$*	All	$H^+NO_2^-$	—	8	$H^+HAsO_4^{=}$	0.1–0.2
	H^+Cl^-	78	90	$H^+H_2PO_4^-$	between	H^+F^-	7	—	$H^+CrO_4^{=}$	0.1–0.2
C	H^+Br^-	79	90	$H^+H_2AsO_4^-$	20–40	$H^+C_2H_3O_2^-$	0.4	1	H^+HS^-	0.07
	H^+I^-	78	90	$H^+HSO_3^-$	per cent	$H^+SO_3^{=}$	—	1–2	H^+CN^-	0.01
I	$H^+HSO_4^-$	—	90	$H^+HC_2O_4^-$	dissociated	$H^+C_2O_4^-$	—	1–2	$H^+AsO_2^-$	(*ca.*)0.005
	$H^+H_3Fe(CN)_6^-$	—	90			$H^+HCO_3^-$	—	0.17	$H^+CO_3^{=}$	" 0.005
D	$H^+H_2Fe(CN)_6^-$	—	90			$H^+HPO_4^-$	—	0.1–0.2	H^+ClO^-	" 0.005
	$H^+HCrO_4^-$	—	90						$H^+PO_4^{\equiv}$	" 0.0001
S	$H^+ClO_4^-$	—	90						H^+S^-	" 0.0001
									$H^+AsO_4^{\equiv}$	" 0.0001

	Strong			Moderate		Weak				
	Ions	*N*	*N/10*	*Ions*	*N/10*	*Ions*	*N*	*N/10*	*Ions*	*N/10*
B A S E S	K^+OH^-	77	90			$NH_4^+OH^-$	0.37	1.0		
	Na^+OH^-	73	90							
	$Ba^{++}2OH^-$	—	80							
	$Ca^{++}2OH^-$	—	80							
S A L T S	B^+A^-(type) (KCl)	76	86			H^+OH^- = Less than 0.000,000,2				
	$2B^+A^=$(type) (Na_2SO_4)	55	72							
	$B^{++}2A^-$(type) ($BaCl_2$)	60	77							
	$B^{+++}3A^-$(type) ($CrCl_3$)	—	65							
	$3B^+A^{\equiv}$(type) ($K_3Fe(CN)_6$)	—	65							

* In such cases as H^+, $SO_4^=$, etc., the degree of ionization is shown on the basis that the two ions are present in equal quantities.

APPENDIX V

REACTIONS OF THE METALS*

GROUP I

Reagent	*Silver* $AgNO_3$	*Mercury (-ous)* $Hg_2(NO_3)_2$	*Lead* $Pb(NO_3)_2$
Hydrochloric Acid. HCl.	Silver Chloride. $AgCl$. White pr., insol. in acids, soluble in NH_4OH, in KCN, in $Na_2S_2O_3$. Darkens in the light.	Mercurous Chloride. Hg_2Cl_2 White pr., sol. in HNO_3, in aqua regia. Converted to $NH_2HgCl + Hg$ by NH_4OH.	Lead Chloride. $PbCl_2$. White pr., slightly soluble in cold water, more easily in hot water. Converted to an insoluble basic salt by NH_4OH.
Hydrogen Sulphide. H_2S.	Silver Sulphide. Ag_2S. Black pr., insol. in $(NH_4)_2S$. Sol. in hot HNO_3.	Mercuric Sulphide and Mercury. $HgS + Hg$. Black pr., partly sol. in HNO_3. Sol. in aqua regia.	Lead Sulphide. PbS. Black pr., insol. in $(NH_4)_2S$. Sol. in HNO_3.
Sulphuric Acid. H_2SO_4.	Silver Sulphate. Ag_2SO_4. White precip., only in concentrated solutions.	Mercurous Sulphate, Hg_2SO_4. White pr., slightly sol. in water.	Lead Sulphate. $PbSO_4$ White pr., insol. in excess, slightly sol. in HNO_3. Sol. in $NH_4C_2H_3O_2$.
Sodium Hydroxide. $NaOH$.	Silver Oxide. Ag_2O. Brown pr., sol. in HNO_3, in NH_4OH.	Mercurous Oxide. Hg_2O. Black pr., soluble in HNO_3, insol. in NH_4OH.	Lead Hydroxide. $Pb(OH)_2$. White pr., sol. in excess, in HNO_3, insol. in NH_4OH.
Ammonium Hydroxide. NH_4OH.	Silver Oxide. Ag_2O. Brown precip., soluble in excess.	Ammonobasic Mercuric Salt and Mercury. Black precip., insol. in excess.	Basic Salt. White pr., insol. in excess.
Sodium Carbonate. Na_2CO_3.	Silver Carbonate. Ag_2CO_3. White precip., soluble in NH_4OH.	Basic Salt. Yellow pr., quickly becoming black.	Basic Lead Carbonate. $2PbCO_3Pb(OH)_2$. White pr., "White Lead."
Potassium Chromate. K_2CrO_4.	Silver Chromate. Ag_2CrO_4. Dark red precip., soluble in HNO_3, in NH_4OH.	Mercurous Chromate. Hg_2CrO_4. Dark red pr.	Lead Chromate. $PbCrO_4$. Yellow pr. Slightly sol. in HNO_3. Sol. in $NaOH$.
Potassium Ferrocyanide. $K_4Fe(CN)_6$.	Silver Ferrocyanide. $Ag_4Fe(CN)_6$. White precip., insoluble in NH_4OH.	Mercurous Ferrocyanide. $Hg_4Fe(CN)_6$. White precipitate.	Lead Ferrocyanide. $Pb_2Fe(CN)_6$. White precipitate.
Stannous Chloride. $SnCl_2$.	Silver Chloride. $AgCl$. White precip.	Mercury. Hg. Dark gray precip.	Lead Chloride. $PbCl_2$. White precipitate.

*These tables with a few minor changes are taken with permission from W. A. Noyes, *Qualitative Analysis* (Henry Holt—1923 Edition).

REACTIONS OF THE METALS

Group II — A. The Copper Group

Reagent	*Mercury (-ic)* $HgCl_2$	*Copper* $CuSO_4$	*Bismuth* $BiCl_3$	*Cadmium* $CdSO_4$
Hydrogen Sulphide. H_2S.	Mercuric Sulphide. HgS. First white, then yellow, reddish brown and black pr., insol. in HNO_3, in $(NH_4)_2S$. Sol. in aq. regia, in $Na_2S + NaOH$.	Copper Sulphide. CuS. Black pr., sol. in HNO_3, in KCN. Very slightly sol. in $(NH_4)_2Sx$ Insol. in hot dil. H_2SO_4.	Bismuth Sulphide. Bi_2S_3. Dark brown pr. sol. in HNO_3, insol. in $(NH_4)_2S$.	Cadmium Sulphide. CdS. Yellow pr. sol. in HNO_3, in hot diluted H_2SO_4, insol. in $(NH_4)_2S$.
Sulphuric Acid. H_2SO_4.	No precipitate.	No precipitate.	No precipitate.	No precipitate.
Ammonium Hydroxide. NH_4OH.	Ammonobasic Mercuric Chloride. $HgNH_2Cl$. White precip.	Basic Copper salt. Greenish blue pr. sol. in excess to a blue solution.	Bismuthyl Hydroxide. BiO OH. White pr., insol. in excess.	Cadmium Hydroxide. $Cd(OH)_2$. White precip., sol. in excess.
Sodium Hydroxide. NaOH.	Mercuric Oxide. HgO. Yellow pr. In presence of NH_4Cl, white pr. of $HgNH_2Cl$.	Copper Hydroxide. $Cu(OH)_2$. Blue pr. changed to black CuO by boiling.	Bismuthyl Hydroxide. BiO OH. White precip.	Cadmium Hydroxide. $Cd(OH)_2$. White precip.
Sodium Carbonate. Na_2CO_3.	Mercuric Oxychloride. $HgCl_2 + nHgO$. Reddish br. pr., changed to yellow HgO by boiling.	Basic Copper Carbonate. Blue pr. changed to black CuO by boiling.	Bismuthyl Carbonate. $(BiO)_2CO_3$. White precip.	Cadmium Carbonate. $CdCO_3$. White precip.
Potassium Chromate K_2CrO_4.	Mercuric Chromate. $HgCrO_4$. Reddish yellow pr., soluble in HNO_3.	Copper Chromate. $CuCrO_4$. Reddish brown precip., sol. in NH_4OH to a green solution.	Bismuthyl Dichromate. $(BiO_2)Cr_2O_7$. Yellow pr., sol. in $HC_2H_3O_2$.	———
Potassium Ferrocyanide $K_4Fe(CN)_6$	———	Copper Ferrocyanide. $Cu_2Fe(CN)_6$. Reddish brown pr. slightly sol. in NH_4OH, insol. in $HC_2H_3O_2$.	Bismuth Ferrocyanide. White pr., insol. in HCl.	Cadmium Ferrocyanide. $Cd_2Fe(CN)_6$. Yellowish white precip., sol. in HCl.
Stannous Chloride. $SnCl_2$.	Mercurous Chloride. Hg_2Cl_2. White pr. An excess of $SnCl_2$ gives gray Hg.	Cuprous Chloride. Cu_2Cl_2. White precip., only in conc. solutions.	Darkens a pr. of BiOOH, changing it to Bi.	———
Water. H_2O.	———	———	Basic Bismuth Salt. BiOCl. White pr., sol. in HCl.	———

Group II — B. The Tin Group

Reagent	*Arsenic*		*Antimony*		*Tin*		*Platinum* H_2PtCl_6	*Gold* $HAuCl_4$
	Arsenious Salts K_3AsO_3	*Arsenic Salts* KH_2AsO_4	*Antimonious Salts* $SbCl_3$	*Antimonic Salts* $KSbO_3$	*Stannous Salts* $SnCl_2$	*Stannic Salts* $SnCl_4$		
Hydrogen Sulphide. H_2S.	Arsenic trisulphide As_2S_3. Yellow pr., sol. in alkalies and alkali sulphides. Insol. in conc. HCl.	Arsenic trisulphide and sulphur. $As_2S_3 + 2S$. Yellow precip. forming slowly and on warming.	Antimony trisulphide. Sb_2S_3. Orange pr., sol. in conc. HCl, in alkalies and alkali sulphides.	Antimony pentasulphide. Sb_2S_5. Orange pr., sol. in conc. HCl, in alkalies and alkali sulphides.	Stannous Sulphide. SnS. Dark brown pr., sol. in conc. HCl in alkalies. Difficultly sol. in yellow $(NH_4)_2S$.	Stannic Sulphide. SnS_2. Yellow pr., sol. in conc. HCl in alkalies and alkali sulphides, in alkali carbonates.	Platinic Sulphide. PtS_2. Dark brown pr., insol. in conc. HCl. Difficultly sol. in alkali sulphides. Sol. in aqua regia.	Gold Sulphide. Au_2S_3 Black pr., insol. in conc. HCl. Sol. in alkali sulphides, sol. in aqua regia.
Ammonium Sulphide. $(NH_4)_2S$.	Arsenic trisulphide. As_2S_3. Only in acid solutions. Sol. in excess.	Arsenic pentasulphide. As_2S_5. Only in acid solutions. Sol. in excess.	Antimony trisulphide. Sb_2S_3. Sol. in excess.	Antimony pentasulphide. Sb_2S_5. Sol. in excess.	Stannous Sulphide. SnS. Sol. in yellow $(NH_4)_2S$.	Stannic Sulphide. SnS_2. Sol. in excess.	Platinic Sulphide. PtS_2. Sol. in excess.	Gold Sulphide. Au_2S_3. Sol. in excess.
Sodium Hydroxide. NaOH.	———	———	Antimonious Hydroxide. $Sb(OH)_3$. White pr., sol. in excess.	Sodium Metantimonate. $NaSbO_3$. White pr., sol. in excess.	Stannous Hydroxide. $Sn(OH)_2$. White pr., sol. in excess.	Stannic Hydroxide. $Sn(OH)_4$. White pr., sol. in excess.	———	———
Potassium Hydroxide. KOH.	———	———	Antimonious Hydroxide. $Sb(OH)_3$. See NaOH	See NaOH	Stannous Hydroxide. $Sn(OH)_2$.	Stannic Hydroxide. $Sn(OH)_4$.	Potassium Chloroplatinate. K_2PtCl_6. Yellow pr. in presence of free HCl.	———
Ammonium Hydroxide. NH_4OH.	———	———	Antimonious Hydroxide. $Sb(OH)_3$. Insol. in excess.	Ammonium Metantimonate. NH_4SbO_3. Nearly insol. in excess.	Stannous Hydroxide. $Sn(OH)_2$. Insol. in excess. Darkens on boiling.	Stannic Hydroxide. $Sn(OH)_4$. Slightly sol. in excess.	Ammonium Chloroplatinate. $(NH_4)_2PtCl_6$. Yellow pr., sol. in great excess.	Fulminating Gold. $\left[Au\begin{smallmatrix}(NH_3)_2\\(OH)_2\end{smallmatrix}\right]OH$. Yellow pr., insol. in excess.
Sodium Carbonate. Na_2CO_3.	———	———	Antimonious Hydroxide. $Sb(OH)_3$. Sol. in excess on boiling.	———	Stannous Hydroxide. $Sn(OH)_2$. Insol. in excess.	Stannic Hydroxide. $Sn(OH)_4$. Slightly sol. in excess.	———	———
Silver Nitrate. $AgNO_3$.	Silver Arsenite. Ag_3AsO_3. Yellow pr., sol. in HNO_3, in NH_4OH.	Silver Arsenate. Ag_3AsO_4. Reddish brown pr., sol. in HNO_3, in NH_4OH.	Silver Chloride and Antimony trioxide. $AgCl + Sb_2O_3$. White precip.	Silver Antimonate. $AgSbO_3$. White pr., sol. in NH_4OH.	Silver Chloride and Silver. $AgCl + Ag$.	Silver Chloride. $AgCl$.	Silver Chloride and Platinum Oxide. $AgCl + PtO_2$. Brown precipitate.	Silver Chloride and Gold Oxide. $AgCl + Au_2O_3$. Brown precipitate.
Copper Sulphate. $CuSO_4$.	Copper Arsenite. $Cu_3(AsO_3)_2$. Yellowish green, pr. sol. in HNO_3, in NH_4OH, in NaOH.	Copper Arsenate. $Cu_3(AsO_4)_2$. Greenish blue pr., soluble in HNO_3, in NH_4OH.	Antimony Oxychloride. SbOCl. White pr. caused by dilution.	Copper Antimonate. Brown precip.	Cuprous Chloride. Cu_2Cl_2. White pr., sol. in acids.	———	———	———
Mercuric Chloride. $HgCl_2$.	Mercuric Arsenite. $Hg_3(AsO_3)_2$. White pr., sol. in acids.	———	Antimony Oxychloride. Caused by dilution. Sol. in conc. HCl.	———	Mercurous Chloride. Hg_2Cl_2. White pr., insol. in cold conc. HCl.	———	———	———
Stannous and Stannic Chlorides. $SnCl_2 + SnCl_4$.	———	———	———	———	———	———	———	Purple of Cassius. Purple-red precip. or coloration.
Magnesia Mixture. NH_4Cl, NH_4OH, $MgCl_2$.	———	Magnesium Ammonium Arsenate. $MgNH_4AsO_4$. White crys. pr., sol. in $C_2H_4O_2$.	Same pr. as by NH_4OH.	Same precip. as by NH_4OH.	Same precip. as by NH_4OH.	Same precip. as by NH_4OH.	Same precip. as by NH_4OH.	Same precip. as by NH_4OH.
Metallic Zinc and Hydrochloric Acid. (Marsh's test.)	Hydrogen and Hydrogen Arsenide. The flame deposits a spot on porcelain. Sol. in sodium hypochlorite. Sol. in $(NH_4)_2S$; on evaporation the yellow residue is insol. in conc. HCl.		Hydrogen and Hydrogen Antimonide. The flame deposits a spot on porcelain. Insol. in sodium hypochlorite. Sol. in $(NH_4)_2S$. On evaporation the orange residue is sol. in conc. HCl.		Metallic Tin.	In neutral solution, also Stannic Hydroxide.	Platinum. Black precipitate.	Gold. Brown precipitate.

Group III

Reagent	*Aluminum* $KAl(SO_4)_2$	*Chromium* $KCr(SO_4)_2$	*Zinc* $ZnCl_2$	*Manganese* $MnCl_2$	*Ferric Salts* $FeCl_3$	*Ferrous Salts* $FeCl_2$	*Cobalt* $CoCl_2$	*Nickel* $NiCl_2$	*Uranium* $UO_2(NO_3)_2$
Ammonium Sulphide. $(NH_4)_2S$.	Aluminum Hydroxide. $Al(OH)_3$. White flocculent pr.	Chromium Hydroxide. $Cr(OH)_3$. Grayish green pr.	Zinc Sulphide. ZnS. White pr. insol. in $C_2H_4O_2$. Sol. in HCl.	Manganese Sulphide. MnS. Flesh-col'd pr. sol. in HCl, in $C_2H_4O_2$. Oxidizes in the air.	Iron Sulphide. Fe_2S_3. Black pr. sol. in acids to a ferrous salt.	Iron Sulphide. FeS. Black pr. sol. in HCl, in $C_2H_4O_2$. Oxidizes in the air.	Cobalt Sulphide. CoS. Black pr. insol. in $C_2H_4O_2$, very slowly sol. in HCl. Sol. in aq. reg.	Nickel Sulphide. NiS. Black pr. slightly sol. in exc. very slowly sol. in HCl. Sol. in aq. reg.	Uranyl Sulphide. UO_2S Dark brown pr. somewhat sol. in exc. of colorless $(NH_4)_2S$.
Hydrogen Sulphide. H_2S.	——	——	Zinc Sulphide. Only in neutral alkaline acid or acetic acid solution.	Manganese Sulphide. Only in neutral or alkaline solutions.	Reduced to a ferrous salt with separation of sulphur.	No pr. in acid solution.	Cobalt Sulphide. Only in neutral or alkaline solutions.	Nickel Sulphide. Only in neutral or alkaline solutions.	——
Ammonium Hydroxide. NH_4OH.	Aluminum Hydroxide. $Al(OH)_3$. White flocculent pr. very slightly sol. in excess.	Chromium Hydroxide. $Cr(OH)_3$. Grayish blue or green precip. slightly sol. in excess with a red color.	Zinc Hydroxide, $Zn(OH)_2$. White pr. sol. in excess. In presence of NH_4Cl no pr.	Manganese Hydroxide. $Mn(OH)_2$. White pr. becoming brown. In presence of NH_4Cl a dark brown pr. forms slowly by oxidation.	Ferric Hydroxide. $Fe(OH)_3$. Reddish brown pr. insol. in excess.	Ferrous Hydroxide. $Fe(OH)_2$. White pr. becoming green and reddish brown. In presence of NH_4Cl, $Fe(OH)_3$ forms slowly.	Basic Salt. Blue pr. sol. in excess to a red sol. In presence of NH_4Cl, no pr.	Nickel Hydroxide. $Ni(OH)_2$. Green pr. sol. in excess to a blue sol. in presence of NH_4Cl no pr.	Ammonium Uranate. $(NH_4)_2U_2O_7$. Yellow pr.
Sodium Hydroxide. $NaOH$.	Aluminum Hydroxide. $Al(OH)_3$. White pr. sol. in excess as $NaAlO_2$.	Chromium Hydroxide. $Cr(OH)_3$. Sol. in excess to a green sol. reprecipitated by boiling.	Zinc Hydroxide $Zn(OH)_2$. White pr. sol. in excess. Reprecipitated by boiling.	Manganese Hydroxide. $Mn(OH)_2$. White pr. becoming brown. Insol. in excess.	Ferric Hydroxide. $Fe(OH)_3$. Reddish brown pr. insol. in excess.	Ferrous Hydroxide. $Fe(OH)_2$. White pr. becoming green and reddish brown, insol. in excess.	Basic Salt. Blue pr. insol. in excess. Sol. in $C_2H_4O_2$, in NH_4OH.	Nickel Hydroxide. $Ni(OH)_2$. Apple green pr. insol. in excess, sol. in $C_2H_4O_2$. in NH_4OH.	Sodium Uranate. $Na_2U_2O_6$. Yellow pr. sol. in $(NH_4)_2CO_3$.
Barium Carbonate. $BaCO_3$.	Aluminum Hydroxide. $Al(OH)_3$. White pr.	Basic Salt. Greenish pr.	No pr. in the cold except in presence of a sulphate.	No pr. in the cold except in presence of a sulphate.	Basic Salt. Reddish brown pr.	No pr. in the cold except in the presence of a sulphate.	No pr. in the cold except in presence of a sulphate.	No pr. in the cold except in presence of a sulphate.	Uranyl Hydroxide. $UO_2(OH)_2$. Yellow pr.
Sodium Phosphate. Na_2HPO_4.	Aluminum Phosphate. $AlPO_4$. White pr. sol. in NaOH, insol. in $C_2H_4O_2$.	Chromium Phosphate. $CrPO_4$. Green pr.	Zinc Phosphate. $Zn_3(PO_4)_2$. White pr. sol. in excess.	Manganese Phosphate. $Mn_3(PO_4)_2$. White pr. sol. in NH_4OH.	Ferric Phosphate. $FePO_4$. Yellowish white pr. sol. in excess. Insol. in $C_2H_4O_2$.	Ferrous Phosphate. $Fe_3(PO_4)_2$. White pr. becoming blue in the air.	Cobalt Phosphate. $Co_3(PO_4)_2$. Red pr. sol. in NH_4OH.	Nickel Phosphate. $Ni_3(PO_4)_2$. Green pr. sol. in NH_4OH.	Uranyl Phosphate. UO_2HPO_4. Yellowish white pr.
Ammonium Carbonate. $(NH_4)_2CO_3$.	Aluminum Hydroxide. $Al(OH)_3$. White pr.	Chromium Hydroxide. $Cr(OH)_3$. Grayish green pr. sol. excess.	Basic Zinc Carbonate. White pr. sol. in excess.	Manganese Carbonate. $MnCO_3$. White pr. insol. in excess.	Basic Salt. Reddish brown pr.	Ferrous Carbonate. $FeCO_3$. White pr. sol. in excess.	Basic Carbonate. Pink pr. sol. in excess.	Basic Carbonate. Green pr. sol. in excess.	Ammonium Uranyl Carbonate. $2(NH_4)_2CO_3 + UO_2CO_3$. Yellow pr. sol. in excess, reprecipitated by alkalies.
Potassium Ferrocyanide. $K_4Fe(CN)_6$.	White pr. forms slowly.	——	Zinc Ferrocyanide. $Zn_2Fe(CN)_6$. White pr. sol. in HCl.	Manganese Ferrocyanide. $Mn_2Fe(CN)_6$. Reddish white precip. sol. in HCl.	Ferric Ferrocyanide. $Fe_4[Fe(CN)_6]_3$. Dark blue pr. insol. in HCl. Decomposed by NaOH.	Ferrous Ferrocyanide. $Fe_2Fe(CN)_6$. Bluish white pr. becoming blue.	Cobalt Ferrocyanide. $Co_2Fe(CN)_6$. Green pr. becoming greenish blue, insol. in HCl.	Nickel Ferrocyanide. $Ni_2Fe(CN)_6$. Greenish white pr. insol. in HCl.	Uranyl Ferrocyanide $[UO_2]_2(Fe[CN]_6)$. Reddish brown pr.
Potassium Ferricyanide. $K_3Fe(CN)_6$.	——	——	Zinc Ferricyanide. $Zn_3(Fe[CN]_6)_2$. Yellowish brown pr. sol. in HCl.	Manganese Ferricyanide. $Mn_3(Fe[CN]_6)_2$. Brown pr. insol. in HCl.	Reddish brown color.	Ferrous Ferricyanide. $Fe_3(Fe[CN]_6)_2$. Dark blue pr. insol. in HCl. Decomposed by NaOH.	Cobalt Ferricyanide. $Co_3(Fe[CN]_6)_2$. Dark brown pr. insol. in HCl.	Nickel Ferricyanide. $Ni_3(Fe[CN]_6)_2$. Yellowish green pr. insol. in HCl.	——
Potassium Thiocyanate. $KCNS$.	——	——	——	——	Blood-red solution. $Fe(CNS)_3$. Most delicate with HCl.	No color.	——	——	Red color.
Borax bead.	——	Yellowish green, hot. Emerald green, cold.	——	Violet red, hot. Amethyst red, cold. Colorless in R.F.	Yellow in O. F. Green in R. F.	Yellow in O. F. Green in R. F.	Blue.	Violet, hot. Reddish brown, cold, gray and turbid in R. F.	Yellow in O. F. Green in R. F.

REACTIONS OF THE METALS

Group IV

Reagent	*Barium* $BaCl_2$	*Strontium* $SrCl_2$	*Calcium* $CaCl_2$	*Magnesium* $MgSO_4$
Ammonium Carbonate. $(NH_4)_2CO_3$.	Barium Carbonate. $BaCO_3$. White pr. sol. in acids.	Strontium Carbonate. $SrCO_3$. White pr. sol. in acids.	Calcium Carbonate. $CaCO_3$. White pr. sol. in acids.	Basic Magnesium Carbonate. $MgCO_3 + nMg(OH)_2$. White pr. on warming and in absence of NH_4 salts.
Sodium Hydroxide. NaOH.	Barium Hydroxide. $Ba(OH)_2$. White pr. only in conc. solutions.	Strontium Hydroxide. $Sr(OH)_2$. White pr. difficultly sol. in water.	Calcium Hydroxide. $Ca(OH)_2$ White pr. difficultly sol. in water.	Magnesium Hydroxide. $Mg(OH)_2$. White pr. sol. in NH_4Cl.
Ammonium Hydroxide. NH_4OH.	No pr.	No pr.	No pr.	Magnesium Hydroxide. $Mg(OH)_2$. Sol. in NH_4Cl.
Sulphuric Acid H_2SO_4	Barium Sulphate. $BaSO_4$. White pr. insol. in water or in acids.	Strontium Sulphate. $SrSO_4$. White pr. very little sol. in water or in $(NH_4)_2SO_4$.	Calcium Sulphate. $CaSO_4$. White pr. somewhat sol. in water. Insol. in alcohol.	———
Ammonium Oxalate. $(NH_4)_2C_2O_4$.	Barium Oxalate. BaC_2O_4. White pr. sol. in HCl, slightly sol. in $C_2H_4O_2$.	Strontium Oxalate. SrC_2O_4. White pr. sol. in HCl, slightly sol. in $C_2H_4O_2$.	Calcium Oxalate. CaC_2O_4. White pr. sol. in HCl, almost insol. in $C_2H_4O_2$ or $H_2C_2O_4$.	No precipitate in dilute solutions.
Potassium Dichromate. $K_2Cr_2O_7$.	Barium Chromate. $BaCrO_4$. Yellow pr. insol. in $C_2H_4O_2$ in presence of $K_2Cr_2O_7$. Sol. in HCl.	Strontium Chromate. $SrCrO_4$. Yellow pr. sol. in $C_2H_4O_2$.	Calcium Chromate. $CaCrO_4$. Yellow pr. sol. in $C_2H_4O_2$.	———
Sodium Phosphate. Na_2HPO_4.	Barium Hydrogen Phosphate. $BaHPO_4$. White pr. sol. in acids.	Strontium Hydrogen Phosphate. $SrHPO_4$. White pr. sol. in acids.	Calcium Hydrogen Phosphate. $CaHPO_4$. White pr. sol. in acids.	Magnesium Hydrogen Phosphate. $MgHPO_4$. White pr. in presence of NH_4OH and NH_4Cl a white cryst. pr. of $MgNH_4PO_4$ is formed. Sol. in $C_2H_4O_2$.
Flame.	Yellowish green.	Bright red.	Yellowish red.	———

REACTIONS OF THE METALS

Group V

Reagent	*Ammonium* NH_4Cl	*Sodium* NaCl	*Potassium* KCl
Sodium Carbonate. Na_2CO_3.	Ammonia. NH_3. On boiling.	———	———
Sodium Phosphate. Na_2HPO_4.	———	———	———
Sodium Cobaltinitrite $Na_3Co(NO_2)_6$	Ammonium Potassium Cobaltinitrite $(NH_4)_2NaCo(NO_2)_6$ Insol. $HC_2H_3O_2$ Sol. HCl	———	Potassium Sodium Cobaltinitrite $K_2NaCo(NO_2)_6$ Insol. $HC_2H_3O_2$ Sol. HCl
Potassium Pyroantimonate. $K_2H_2Sb_2O_7$.	———	Sodium Pyroantimonate. $Na_2H_2Sb_2O_7$. White cryst. pr., best in slightly alkaline solutions.	———
Nessler's Reagent. $K_2HgI_4 + KOH$.	Reddish brown pr. or yellow color, very delicate.	———	———
Sodium Hydroxide. NaOH.	Evolves NH_3 on warming.	———	———
Flame.	———	Yellow.	Violet.

APPENDIX VI

ATOMIC WEIGHTS OF SOME OF THE COMMON ELEMENTS

Aluminum	Al	26.97	Magnesium	Mg	24.32
Antimony	Sb	121.77	Manganese	Mn	54.93
Arsenic	As	74.96	Mercury	Hg	200.61
Barium	Ba	137.37	Nickel	Ni	58.69
Bismuth	Bi	209.00	Nitrogen	N	14.008
Cadmium	Cd	112.41	Oxygen	O	16.00
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.00	Silicon	Si	28.06
Chlorine	Cl	35.46	Silver	Ag	107.88
Chromium	Cr	52.01	Sodium	Na	23.00
Cobalt	Co	58.94	Sulphur	S	32.06
Copper	Cu	63.57	Tin	Sn	118.70
Hydrogen	H	1.008	Zinc	Zn	65.38
Iron	Fe	55.84			
Lead	Pb	207.22			

APPENDIX

REACTIONS OF THE

Salts of	*Barium Chloride*	*Calcium Chloride*	*Silver Nitrate*
Sulphuric Acid. H_2SO_4.	White pr. insol. in acids.	White pr. somewhat sol. in water and in acids.	White pr. only in conc. solutions.
Hydrofluosilicic Acid. H_2SiF_6.	White pr. insol. in HCl.	———	———
Sulphurous Acid. H_2SO_3.	White pr. sol. in HCl.	White pr. sol. in HCl.	White pr. decomposed by boiling into Ag, Ag_2SO_4 and SO_2.
Phosphoric Acid. H_3PO_4.	White pr. sol. in acids.	White pr. sol. in acids, even in $HC_2H_3O_2$.	Yellow pr. sol. in HNO_3, in NH_4OH.
Arsenic Acid. H_3AsO_4.	White pr. sol. in acids.	White pr. sol. in $HC_2H_3O_2$.	Reddish brown pr. sol. in HNO_3, in NH_4OH.
Arsenious Acid. H_3AsO_3.	White pr. sol. in acids.	White pr. sol. in $HC_2H_3O_2$.	Yellow pr. sol. in HNO_3, in NH_4OH.
Chromic Acid. H_2CrO_4.	Yellow pr. sol. in HCl, in HNO_3, insol. in $HC_2H_3O_2$.	———	Dark red pr. sol. in HNO_3.
Boric Acid. $H_3BO_3(H_2B_4O_7)$	White pr. difficulty sol. in water, sol. in acids.	White pr. sol. in acids.	White pr. sol. in HNO_3, in NH_4OH.
Silicic Acid. H_2SiO_3.	White pr.	White pr.	Yellow pr. sol. in conc. solutions, sol. in HNO_3.
Carbonic Acid. H_2CO_3.	White pr. sol. in acids.	White pr.	White pr. sol. in HNO_3.
Hydrofluoric Acid. H_2F_2.	White pr. sol. in hot HCl.	White, gelatinous pr., sol. in HCl, insol. in $HC_2H_3O_2$.	———
Hydrochloric Acid. HCl	———	———	White pr., insol. in HNO_3, soluble in NH_4OH, in KCN.
Hydrobromic Acid. HBr.	———	———	Yellowish white pr., difficultly sol. in NH_4OH. Insol. in HNO_3.
Hydriodic Acid. HI.	———	———	Yellow precip. insol. in NH_4OH, in HNO_3.

VII

INORGANIC ACIDS

Lead Acetate	*Characteristic Reactions*
Wh. pr. sol. in NaOH, in ammonium tartrate, in am. acetate.	Sulphates when heated with Na_2CO_3, in the reducing flame on charcoal give a hepar (Na_2S) which blackens silver, when moistened with water.
———	The potassium salt is difficultly soluble. Fluosilicates give with conc. H_2SO_4, H_2F_2 and SiF_4.
White pr.	Sulphites reduce $KMnO_4$, give a hepar with Na_2CO_3 on charcoal. Give SO_2 without separation of S, on warming with HCl.
White pr. sol. in NaOH, insol. in NH_4OH.	Added to a solution of ammonium molybdate in HNO_3, gives a yellow pr. of ammonium phosphomolybdate; $MgCl_2 + NH_4OH + NH_4Cl$ precipitate white cryst. $MgNH_4PO_4$.
White pr. sol. in HNO_3 insol. in HCH_3O_2.	Yellow precip. with $(NH_4)_2MoO_4$. White precip. with $NH_4Cl + NH_4OH + MgCl_2$.
White pr. sol. in HNO_3 soluble in $HC_2H_3O_2$.	Marsh's test gives an arsenic mirror. H_2S precipitates yellow As_2S_3 from the warm acid solution.
Yellow pr. sol. in NaOH.	Reduced to green $CrCl_3$ by warming with HCl and alcohol.
White pr. sol. in excess of the lead salt.	With alcohol and conc. H_2SO_4 colors flame green. Turmeric paper dipped in the HCl solution becomes red on drying.
White pr. insol. in HNO_3.	Evolves CO_2 with Na_2CO_3 bead. Gives a skeleton of SiO_2 with $NaPO_3$ bead. SiO_2 separates on evaporating the acid solution to dryness.
White pr. sol. in HNO_3.	Effervesces with HCl giving CO_2 which renders lime water turbid.
White precipitate, sol. in HNO_3.	With conc. H_2SO_4 gives H_2F_2, which etches glass.
White precipitate, soluble in hot water.	With H_2SO_4 and MnO_2 gives Cl_2. With conc. H_2SO_4 and $K_2Cr_2O_7$ gives CrO_2Cl_2.
White precipitate, slightly soluble in hot water.	Cl_2 water liberates Br_2 which dissolves in CS_2 to a reddish-yellow solution.
Yellow precipitate, slightly soluble in hot water.	Cl_2 water, or nitrous acid, liberates I_2, which dissolves in CS_2 to a violet red solution, or colors starch paste blue.

REACTIONS OF THE

Salts of	*Barium Chloride*	*Calcium Chloride*	*Silver Nitrate*
Hydrocyanic Acid. HCN.	———	———	White precip. sol. in NH_4OH, in KCN.
Hydroferrocyanic Acid. $H_4Fe(CN)_6$.	———	———	White pr. soluble in KCN, insoluble in HNO_3.
Hydroferricyanic Acid. $H_3Fe(CN)_6$.	———	———	Orange pr. sol. in NH_4OH, in KCN, insol. in HNO_3.
Thiocyanic Acid. HCNS.	———	———	White precipitate, difficultly sol. in NH_4OH.
Nitrous Acid. HNO_2.	———	———	White pr. sol. in hot water.
Hydrosulphuric Acid. H_2S.	———	———	Black precipitate, soluble in hot HNO_3.
Nitric Acid. HNO_3.	———	———	———
Oxalic Acid. $H_2C_2O_4$	———	White precip., insol. in $HC_2H_3O_2$.	White precip. sol. in HNO_3.

INORGANIC ACIDS (*cont.*)

Lead Acetate	*Characteristic Reactions*
White precipitate, soluble in HNO_3.	After warming with $FeSO_4$, $FeCl_3$ and NaOH, on adding HCl, Prussian blue remains undissolved. When warmed with yellow $(NH_4)_2S$, NH_4CNS is formed.
White precipitate.	Gives Prussian blue with ferric salts. Gives a red precipitate with Cu salts.
No pr. in alkaline solutions, but on warming PbO_2 is precipitated.	Gives a dark blue precipitate with ferrous salts.
White precipitate.	Blood-red color with $FeCl_3$, not destroyed by boiling, but which vanishes on adding $HgCl_2$.
———	Gives a yellow color with meta-phenylene-diamine in acid solution.
Black precip. sol. in hot HNO_3.	Sulphides give a hepar with Na_2CO_3. See sulphates. Soluble sulphides give a violet color with Sodium nitroprusssiate.
———	Mixed with $FeSO_4$ and poured on conc. H_2SO_4, gives a dark brown zone. Colors a solution of brucine in H_2SO_4, red.
White precip., sol in HNO_3 and NH_4OH	With dil.H_2SO_4 and MnO_2, gives CO_2.